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(54) **HETEROCYCLIC NITROGENOUS OR OXYGENOUS COMPOUNDS WITH INSECTICIDAL ACTIVITY FORMED FROM DIALDEHYDES AND THEIR PREPARATION AND USES THEREOF**

HETEROCYCLISCHE STICKSTOFF- ODER SAUERSTOFFVERBINDUNGEN MIT INSEKTIZIDER WIRKUNG AUS DIALDEHYDEN SOWIE IHRE HERSTELLUNG UND VERWENDUNG

COMPOSÉS AZOTÉS OU OXYGÉNÉS HÉTÉROCYCLIQUES AYANT UNE ACTIVITÉ INSECTICIDE FORMÉS À PARTIR DE DIALDÉHYDES ET LEUR PRÉPARATION ET LEURS UTILISATIONS

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- **MICHIHIKO N. ET AL.: 'Chirality Transfer in the Ene-reactions of 3-{2-(2S)- [2-(Substituted) vinyl] pyrrolidin-1-yl}-2-(sustituted)acrole in Derivatives.' TETRAHEDRON LETTERS vol. 41, no. 44, 2000, pages 8489 - 8493, XP004236108**

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- MICHIHIKO N. ET AL.: 'Thermal Ene Reactions of3-(Alk-2-enyl)benzylamino -2-(methoxycarbonyl)acrolein Derivatives Leading to 4,5-Dihydro -1H- azepines.' TETRAHEDRON vol. 56, no. 10, 2000, pages 1299 - 1307, XP004190786
- SHAO XUSHENG ET AL.: 'Divalent and Oxabridged Neonicotinoids Constructed by Dialdehydes and Nitromethylene Analogues of Imidacloprid: Design, Synthesis, Crystal Structure, and Insecticidal Activities.' J. AGRICULTURAL AND FOOD CHEMISTRY vol. 58, no. 5, 2010, pages 2696 - 2702, XP008140274

Description

FIELD OF THE INVENTION

[0001] This invention relates to novel neonicotinoid derivatives, the preparation method and the uses thereof.

BACKGROUND OF THE INVENTION

[0002] Represented by Imidacloprid, neonicotinoid insecticide has been act as a hot area of pesticide discovery, with the character of high insecticidal activity, wide insecticidal spectrum, low toxic to mammals and aquatic animals, good systematic properties, appropriate field stability and environmental friendship. After Imidacloprid, a series of neonicotinoid insecticides such as Thiacloprid, Clothianidin, Thiamethoxam, Acetamiprid, Nitenpyram and Dinotefuran were developed (EP 247477, 296453, 685477, 235725, 235725, 315826, 192060, 244777, 0386565, 580553, 1031566, JP 62292765, 8259568, 8291171 and 7242633).

[0003] However, the application and development of these compounds are limited due to the resistance caused by over frequent use of Imidacloprid and cross-resistance among neonicotinoid insecticides caused by structural similarity. Meanwhile, the neonicotinoid insecticides mainly show high activity to Homoptera and Coleoptera pests, and the narrow insecticidal spectrum limits their broad application in pest control.

[0004] Therefore, it is urgent in the art to develop compounds with efficient activities from high active nitromethylene compounds so as to solve the problem of resistance, enlarge the insecticidal spectrum and apply them in insecticide compositions.

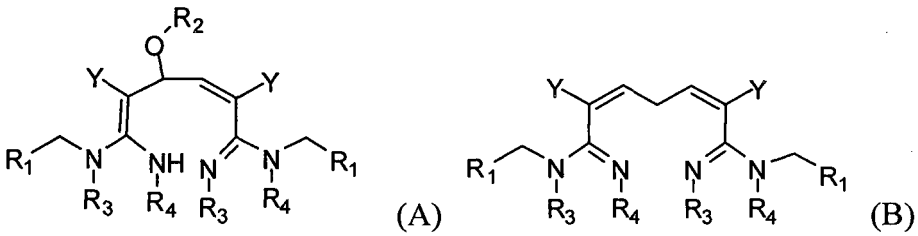
SUMMARY OF INVENTION

[0005] This invention provides novel effective insecticides, which resolve the resistance problem of neonicotinoid insecticides, enlarge the insecticidal spectrum and address the issues existed in the art.

[0006] One object of the invention is to provide derivatives for effective pest control and the preparation thereof.

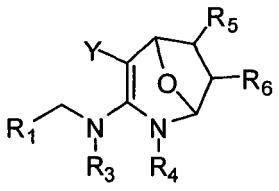
[0007] Another object of the invention is to provide the protection for growing and harvested plants and prevent them from the invading of insect.

[0008] According to the first aspect of the invention, it is provided a compound of formula (A), (B), (C) or (D), its optical isomer, cis-trans isomer, or its agrochemically acceptable salts thereof

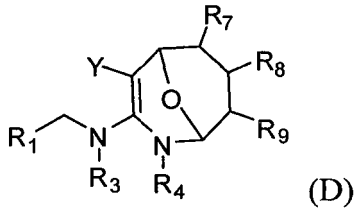


(A)

(B)



(C)



(D)

wherein R_1 is 5 or 6 membered heterocycle containing nitrogen, oxygen and/or sulfur atom, halo-substituted 5 or 6 membered heterocycle containing nitrogen, oxygen and/or sulfur atom, substituted or unsubstituted phenyl, wherein the substituents are one or more groups selected from the group consisting of halogen atoms, C_{1-4} halo-alkyl or C_{1-4} chloro-alkoxyl;

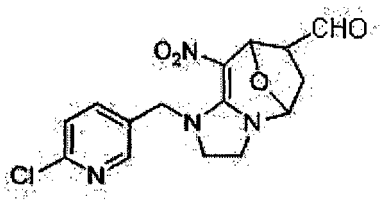
R_2 is H, C_{1-8} saturated or unsaturated alkyl, halo-substituted C_{1-8} saturated or unsaturated alkyl, $-CH_2CH_2OCH_2CH_3$, $-CH_2CH_2OCH_3$, C_{1-4} alkyl-carbonyl, C_{1-4} alkyl-sulfonyl, phenyl, unsubstituted benzyl or substituted benzyl substituted by one or more groups selected from the group consisting of halogen atom, C_1 - C_4 halo-alkyl or C_{1-4} chloro-alkoxyl;

R_3 and R_4 are independently selected from H, C_{1-6} alkyl, allyl, benzyl, C_{1-4} alkoxyl-C_{1-4} alkyl, C_{1-4} alkoxyl-carbonyl, phenoxycarbonyl, C_{2-6} alkynyl-carbonyl, C_{2-3} alkenyl-carbonyl, C_{3-6} cycloalkyl-carbonyl, unsubstitued benzoyl group

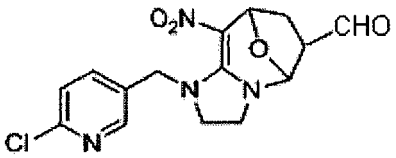
or benzoyl group substituted by one or more groups selected from the group consisting of halogen atoms, C_{1-4} alkyl, C_{1-4} halo-alkyl, C_{1-4} alkoxyl or C_{1-4} alkyl-carbonyl, furan carbonyl or N, N-dimethylaminocarbonyl; or R_3 and R_4 together form $-CH_2-CH_2-$, $-CH_2-CH_2-CH_2-$ or $-CH_2-XR-CH_2-$, wherein X represents N, O, S or other heteroatom; R is substituent on X and selected from H, C_{1-6} alkyl, allyl, benzyl, phenyl, C_{1-4} alkoxyl-C_{1-4} alkyl, C_{1-4} alkoxyl-carbonyl, phenoxycarbonyl, C_{2-6} alkynyl-carbonyl, C_{2-3} alkenyl-carbonyl, C_{3-6} cycloalkyl-carbonyl, unsubstitued benzoyl group or benzoyl group substituted by one or more groups selected from the group consisting of halogen atoms, C_{1-4} halo-alkyl, C_{1-8} saturated or unsaturated alkyl or alkoxyl, or C_{1-4} alkyl-carbonyl, furan carbonyl or N, N-dimethylaminocarbonyl.

R_5, R_6, R_7, R_8 and R_9 are H, saturated or unsaturated C_{1-4} alkyl, halogen, saturated or unsaturated C_{1-8} alkoxyl, saturated or unsaturated C_{1-4} halo-alkoxyl, C_{1-4} alkyl-carbonyl, C_{1-4} alkyl-sulfonyl, phenyl or benzyl;

Y is nitro, cyano, trifluoromethyl, trifluoroacetyl, or trifluoromethylsulfonyl; or the compound is compound No. 71 or compound No. 73;



Compound No. 71

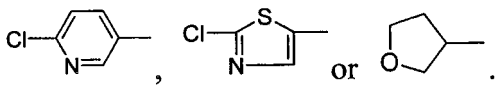


Compound No. 73

[0009] In one embodiment, R_1 is selected from pyridyl, thiazolyl, pyrimidinyl, tetrahydrofuryl, oxazolyl, or the halogenated groups thereof.

[0010] In one embodiment, the preferable R_1 represents halopyridyl, halothiazolyl, halopyrimidinyl, halotetrahydrofuryl, or halooxazolyl. Preferably, the halogenated groups are chlorides.

[0011] In another embodiment, R_1 represents



[0012] In another embodiment, R_2 represents H, saturated or unsaturated C_{1-4} alkyl, saturated or unsaturated C_{1-4} halo-alkyl, C_{1-4} alkyl-carbonyl, unsubstituted benzyl or benzyl substituted by one or more groups selected from the group consisting of halogen atom, C_{1-4} halo-alkyl or C_{1-4} chloro-alkoxyl.

[0013] In one embodiment, R_2 represents H or C_{1-3} alkyl. More preferably, R_2 represents H or methyl.

[0014] In another embodiment, R_3 and R_4 are H, C_{1-6} alkyl, or R_3 and R_4 together form $-CH_2-CH_2-$ or $-CH_2-CH_2-CH_2-$.

[0015] In one embodiment, R_3 and R_4 are hydrogen atom or C_{1-3} alkyl, and preferably H, methyl or ethyl. Alternatively, R_3 and R_4 together form $-CH_2-CH_2-$ or $-CH_2-CH_2-CH_2-$.

[0016] In another embodiment, R_5, R_6, R_7, R_8 and R_9 are H, saturated or unsaturated C_{1-2} alkyl, halogen, saturated or unsaturated C_{1-4} alkoxyl, saturated or unsaturated C_{1-2} halo-alkoxyl, or C_{1-2} alkyl-sulfonyl..

[0017] In one embodiment, R_5, R_6, R_7, R_8 and R_9 represent H, methyl, chloride atom, bromide atom, methoxyl or ethoxyl and preferably represent H, methyl and methoxyl.

[0018] In another embodiment, Y is nitro group or cyano group.

[0019] In one embodiment, Y represents nitro group. Specific embodiments of the present invention are shown in tables 1 to 4.

[0020] According to the second aspect of the invention, it is provided an agrochemical composition comprising:

(a) 0.001-99.99wt% of the above-mentioned compound, its optical isomer, cis-trans isomer, agrochemically acceptable salts thereof or the combination thereof; and
(b) an agrochemically acceptable carrier or excipient.

[0021] In one embodiment, the concentration of component (a) is 0.01-99.9wt%, and preferably 0.05-90wt%.

[0022] In one embodiment, the agrochemical composition is used to kill or control the insects selected from the group consisting of Coleoptera, Lepidoptera, Hemiptera, Orthoptera, Isoptera and dipteral insects.

[0023] In one embodiment, the pests have piercing-sucking type or scratching type mouthparts.

[0024] In another embodiment, the pests comprise aphid, planthopper, white fly, leaf hopper, thrips, cotton bollworm,

Cabbage caterpillar, Diamondback prodenia litura or army worm.

[0025] In another embodiment, the agrochemical composition further comprises other active compounds which are selected from the group consisting of insecticide, cobait, bactericide, acaricide, nematicide, fungicide and growth control agents.

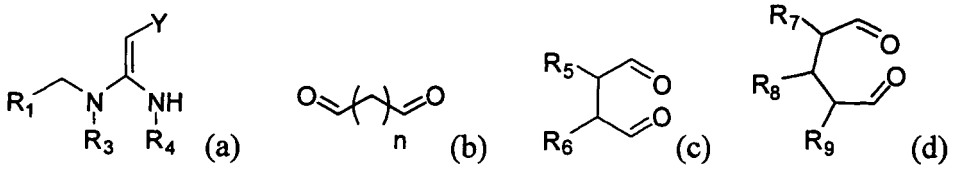
[0026] According to the third aspect of the invention, it is provided the use of the agrochemical composition in killing or controlling agricultural pests, sanitary pests and animal health hazard pests; or the agrochemical composition is used as an insecticidal composition for killing or controlling agricultural pests, sanitary pests, animal health hazard pests, and animal health hazard pests.

[0027] According to the forth aspect of the invention, it is provided a method of for killing or controlling agricultural pests, sanitary pests and animal health hazard pests, wherein the method comprises applying the above agrochemical or insecticidal composition onto plants, their surrounding soil or environment that is attacked or will be attacked by insects.

[0028] According to the fifth aspect of the invention, it is provided the use of the compound, its optical isomer or cis-trans isomer, an agrochemically acceptable salts or their composition in preparation of insecticide composition.

[0029] According to the sixth aspect of the invention, it is provided a method for preparation of the compound, its optical isomer or cis-trans isomer, or agrochemically acceptable salts, wherein the method comprises the following steps:

[0030] In the presence of catalytic acid and at 0-60 °C, reacting compound of formula (a) with compound (b), (c) or (d), thereby forming compound (A), (B), (C) or (D), wherein R_2 represents H,



wherein R_1, R_3, R_4, R_5, R_6, R_7, R_8, R_9 and Y are defined as hereinabove, and n is 0 or 1.

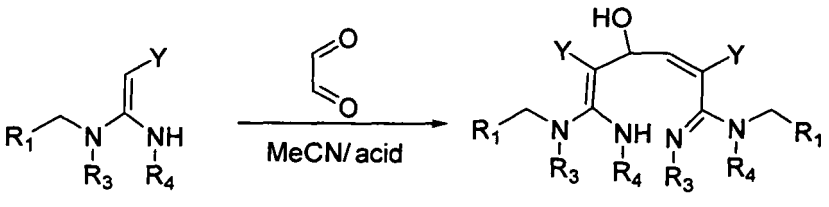
[0031] In one embodiment, the reaction temperature is 15-45 °C, and preferably 20-30 °C.

[0032] In another embodiment, the solvent is chosen from acetonitrile or ethanol, and preferably acetonitrile.

[0033] In another embodiment, the catalytic acid is chosen from concentrated hydrochloric acid, concentrated sulfuric acid or benzoic acid, and preferably concentrated hydrochloric acid.

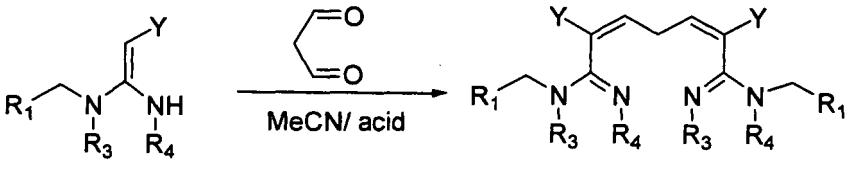
[0034] In one embodiment, the method comprises:

in the presence of catalytic acid, the following reaction is carried out at 20-30 °C in acetonitrile for 2-24 hours, thereby forming compound (A), wherein R_2 is H:



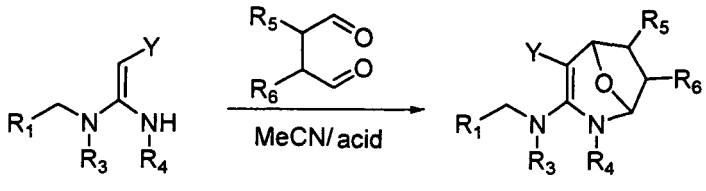
(A);

in the presence of catalytic acid, the following reaction is carried out at 20-30 °C in acetonitrile for 2-24 hours, thereby forming compound (B):



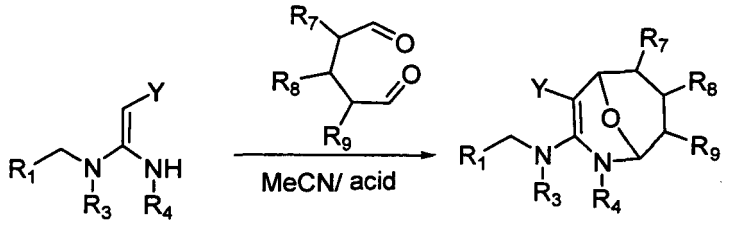
(B);

in the presence of catalytic acid, the following reaction is carried out at 10-50 °C in acetonitrile for 2-24 hours, thereby forming compound (C):



(C);

in the presence of catalytic acid, the following reaction is carried out at 10-50 °C in acetonitrile for 2-24 hours, thereby forming compound (D):



(D).

DETAILED DESCRIPTION OF THE INVENTION

[0035] After long term and deep investigation, the inventors have synthesized a novel class of neonicotinoid derivatives, which are obtained by the reaction of nitromethylene compounds with dialdehyde based on the nitromethylene group of current nitromethylene neonicotinoid insecticides. The novel derivatives show significantly high activities and enlarged insecticidal spectrum. The inventors completed the present invention based on the above.

Definition of Substitutions

[0036] The term "C_{1-6} alkyl" refers to straight or branched alkyl with 1-6 carbon such as methyl, ethyl, propyl, *iso*-propyl, butyl, *iso*-butyl, *sec*-butyl, *tert*-butyl or some similar groups.

[0037] The term "C_{1-6} alkoxyl" refers to straight or branched alkoxyl with 1-6 carbon such as methoxyl, ethoxyl, propoxyl, iso-propoxyl, butoxyl, *iso*-butoxyl, *sec*-butoxyl, *tert*-butoxyl or some similar groups.

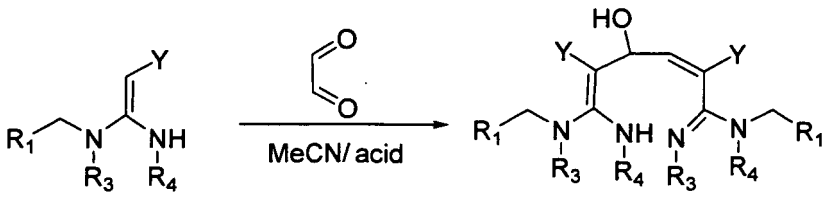
[0038] The term "halogen" refers to fluorine, chlorine, bromine or iodine. The term "halogenated" refers to one or more substitution with same or different "halogen" as mentioned above, such as trifluoromethyl, pentafluoroethyl or similar groups.

[0039] The term "5 or 6 membered heterocyclic alkyl" refers to 5 or 6 membered ring cyclic alkyl containing one or more heteroatoms selected from nitrogen, oxygen or sulfur, such as pyridyl, thiazyl, pyrimidinyl, tetrahydrofuryl, oxazolyl etc.

Preparation of the compound of invention

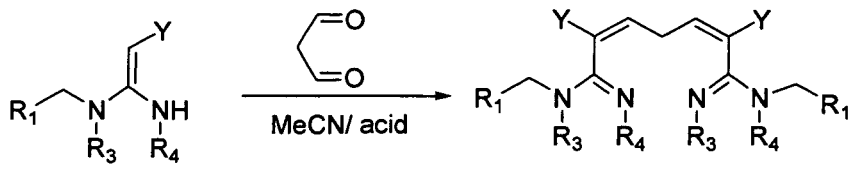
[0040] Compounds of the invention can be synthesized as described above. The compound (a) can be obtained according to the technical references in the art, such as WO2006056108A1, WO2007101369A1 and PCT/CN2008/071115.

[0041] In one embodiment, compound of formula (A) can be synthesized by the following procedure, wherein R_2 is H:



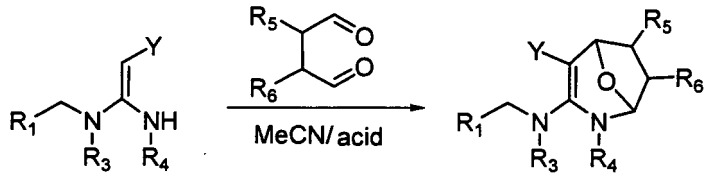
(A);

[0042] In one embodiment, compound of formula (B) can be synthesized by the following procedure:



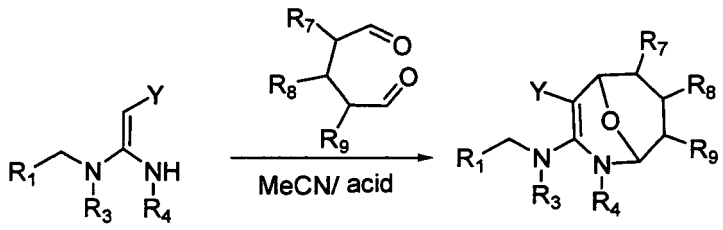
(B);

[0043] In one embodiment, compound of formula (C) can be synthesized by the following procedure:



(C);

[0044] In one embodiment, compound of formula (D) can be synthesized by the following procedure:



(D).

[0045] In one embodiment, compound of formula (A) can be synthesized by the following procedure:

(1) A solution of 2-chloro-5-(chloromethyl)pyridine in acetonitrile is added dropwise to 5-10 mole of diamine solution. The reaction is carried out at 0-50°C for 5-10 hours. After completion, the mixture is distillated under reduced pressure to remove diamine, dissolved in ethyl acetate and evaporated to obtain N-((6-chloropyridin-3-yl)methyl)diamine.
(2) A mixture of N-((6-chloropyridin-3-yl)methyl)diamine and 1,1-dimethylthio-2-nitroethene is dissolved in ethanol and refluxed for 4-8 hours to obtain the nitromethylene compound.
(3) In the presence of acidic catalyst such as hydrochloric acid, sulfuric acid, heteropolyacids etc., nitromethylene compound reacts with oxaldehyde (glyoxal) to obtain compound of formula (A).

[0046] In another embodiment, compound of formula (B) can be synthesized by the following procedure:

(1) To a solution of aqueous ethylamine, an appropriate amount of acetonitrile is added.
Then 2-chloro-5-(chloromethyl)pyridine in acetonitrile is added dropwise in ice bath. The reaction is monitored by TLC. After completion, the mixture is added large amount of water, extracted by DCM, dried, filtered and evaporated to obtain N-((6-chloropyridin-3-yl)methyl)ethenamine as oil.
(2) A mixture of N-((6-chloropyridin-3-yl)methyl)ethenamine and 1,1-dimethylthio-2-nitroethene is dissolved in ethanol and refluxed for 4-8 hours. After completion, the mixture is concentrated and purified by column chromatography to obtain N-((6-chloropyridin-3-yl)methyl)-N-ethyl-1-(methylthio)-2-nitroethenamine.
(3) A mixture of methylamine alcohol solution and N-((6-chloropyridin-3-yl)methyl)-N-ethyl-1-(methylthio)-2-nitroethenamine is dissolved in ethanol and reacted for 4-8 hours in ice bath. After completion, the mixture is concentrated and purified by column chromatography to obtain N-((6-chloropyridin-3-yl)methyl)-N-ethyl-N'-methyl-2-nitroethene-1,1-diamine.
(4) In the presence of acidic catalyst such as hydrochloric acid, sulfuric acid, heteropolyacids etc., N-((6-chloropyridin-3-yl)methyl)-N-ethyl-N'-methyl -2-nitroethene-1,1-diamine reacts with malonaldehyde to obtain compound of formula (B).

[0047] In another embodiment, compound of formula (C) can be synthesized by the following procedure:

(1) A solution of 2-chloro-5-(chloromethyl)pyridine in acetonitrile is added dropwise to 5-10 mole of diamine solution.

The reaction is carried out at 0-50°C for 5-10 hours. After completion, the mixture is distillated under reduced pressure to remove diamine, dissolved in ethyl acetate and evaporated to obtain N-((6-chloropyridin-3-yl)methyl)diamine.
(2) A mixture of N-((6-chloropyridin-3-yl)methyl)diamine and 1,1-dimethylthio-2-nitroethene is dissolved in ethanol and refluxed for 4-8 hours to obtain the nitromethylene compound.
(3) In the presence of acidic catalyst such as hydrochloric acid, sulfuric acid, heteropolyacids etc., nitromethylene compound reacts with succinaldehyde to obtain compound of formula (C).

[0048] In another embodiment, compound of formula (D) can be synthesized by the following procedure:

(1) A solution of 2-chloro-5-(chloromethyl)pyridine in acetonitrile is added dropwise to 5-10 mole of diamine solution. The reaction is carried out at the temperature range of 0-50°C for 5-10 hours. After completion, the mixture is distillated under reduced pressure to remove diamine, dissolved in ethyl acetate and evaporated to obtain N-((6-chloropyridin-3-yl)methyl)diamine.
(2) A mixture of N-((6-chloropyridin-3-yl)methyl)diamine and 1,1-dimethylthio-2-nitroethene is dissolved in ethanol and refluxed for 4-8 hours to obtain the nitromethylene compound.
(3): In the presence of acidic catalyst such as hydrochloric acid, sulfuric acid, heteropolyacids etc., nitromethylene compound reacts with glutaraldehyde to obtain compound of formula (D).

Insecticidal Activity Of Active Compounds Of Invention

[0049] The terms "active ingredient of the invention" or "active compound of the invention" represent the invented compound, its optical isomer or cis-trans isomer, or an agrochemically acceptable salts thereof. The "active compound of the invention" shows significantly increased activities and broadened insecticidal spectrum.

[0050] The term "agrochemically acceptable salts" means that the anion of the salt is known or acceptable when forming the insecticidally acceptable salt. Preferably, the salt is water-soluble. The salts formed by the compounds of formula (A), (B), (C) and (D) include salts formed with inorganic acid (e.g., hydrochlorate, phosphate, sulfate, and nitrate) and salts formed with organic acid (e.g., acetate and benzoate).

[0051] The active compound of this invention can be used to control and kill general agriculture and plant insects, storage cereal insects, public health insects and animal health hazard insects. In this invention, term "insecticide" represents any compound that prevents or controls any of the above mentioned insects. The exemplary insects include but are not limited to: Coleoptera: *Sitophilus zeamai, Tribolium castaneum, Henosepilachna vigintioctomaculata, Henosepilachna spars. Agriotes fuscicollis, Anomala cupripes, Popillia quadriguttata, Monolepta hieroglyphica, Monochamus alternatus, Echinocnemus squameus, Basiprionota bisignata, Anoplophora chinensis, Apripona germari, Scolytus schevy, Agriotes fuscicollis.*

Lepidoptera: *Lymantria dispar, Malacosoma neustria testacea, Diaphania perspectalis, Clania variegate, Cnidocampa flauescens, Dendrolimus punctatus, Orgyia gonostigma, Paranthrene tabaniformis, Spodoptera litura, Chilo suppressalis, Ostrinia nubilalis, Ephestia cautella, Adoxophyes orana, Laspyresia splendana, Agrotis fucosa, Galleria mellonella, Plutella xylostella, Phyllocnistis citrella,* or *Mythimna separate.*
Homoptera: *Nephotettix cincticeps, Nilaparvata lugens, Pseudococcus comstocki, Unaspis yanonensis, Myzus persicae, Aphis gossydii, Lipaphis erysimi pseudobrassicae, Stephanitis nashi,* or *Bemisia tabaci.*
Orthoptera: *Blattella germanica, Periplaneta americana, Gryllotalpa africana,* or *Locusta migratoria.*
Isoptera: *Solenopsis invicta, Coptotermes formosanus.*
Diptera: *Musca domestica, Aedes aegypti, Delia platura, Culex sp., Anopheles sinensis.*
Animal Health hazard insects: *Boophilus microplus, Haemaphysalis longicornis, Hyalomma anatolicum, Hypoderma spp., Fasciola hepatica, Moniezia Blanchard, Ostertagia spp., Trypanosoma enansi, Babesia bigemina,* etc.

[0052] The compounds of the invention have specific effects on agriculture and plant insects having a piercing-sucking or scratching monthparts, such as aphid, leafhopper, planthopper, thrips, white fly and so on.

Insecticidal Composition Containing Compound Of Invention

[0053] The invented active compounds can be generally prepared into insecticidal composition. The invented active compounds can be prepared into the conventional formulations, such as solutions, emulsions, suspensions, powders, foams, pastes, granules, aerosols, natural and synthetic materials impregnated with active compounds, and microcapsules in polymers, the coating complex for seed, preparations used with a combustion device (such as smoking cylindrantherae, smoking can and smoking plate) and ULV cold mist and warm mist preparations.

[0054] These formulations may be produced in a known manner, for example, by mixing the active compounds with

extenders, which are liquid or liquefied gaseous, solid diluents or carriers, optionally with the use of surface-active agents, which is emulsifying agents and/or dispersing agents, and/or foam-forming agents. In the case of using water as an extender, organic solvents can also be used as auxiliary solvents.

[0055] It is generally proper to use liquid solvents as a diluent or carrier, for example, aromatic hydrocarbons, such as xylene, toluene and alkyl naphthalenes; chlorinated aromatic or chlorinated aliphatic hydrocarbons, such as chlorobenzenes, chloroethylenes and methylene chloride; aliphatic hydrocarbons, such as cyclohexane or paraffins, for example, mineral oil fractions; alcohols, such as ethanol or glycol as well as their ethers and esters; ketones, such as acetone, methyl ethyl ketone, methyl isobutyl ketone or cyclohexanone; or uncommon polar solvents, such as dimethylformamide and dimethylsulfoxide, as well as water. By liquefied gaseous diluents or carriers are meant liquids which are gaseous at normal temperature under normal pressure, for example, aerosol propellants, such as halogenated hydrocarbons as well as butane, propane, nitrogen and carbon dioxide.

[0056] The solid carrier comprises ground natural minerals, such as kaolins, clays, talcs, quartzs, attapulgites, montmorillonites or kieselguhrs; ground synthetic minerals, such as high dispersed silicic acid, alumina and silicate. The solid carrier used for particles is crushed and fractionated natural rocks such as calcite, marble, pumice, sepiolite and dolomite, as well as synthetic granules of inorganic and organic coarse powder, and granules of organic material such as sawdust, coconut shells, maize cobs and tobacco stalks and the like.

[0057] Nonionic and anionic emulsifiers may be used as emulsifying and/or foam-forming agents, such as polyoxyethylene-fatty acid esters, polyoxyethylene-fatty alcohol ethers, for example, alkylaryl polyglycol ethers, alkylsulfonates, alkylsulfates, arylsulfonates as well as albumin hydrolysis products. Dispersing agents include, for example, lignin sulfite waste liquors and methyl cellulose.

[0058] Adhesives such as carboxymethyl cellulose and natural and synthetic polymers, (such as gum arabic, polyvinyl alcohol and polyvinyl acetate) in the form of powders, granules or emulsions can be used in the formulations. It is possible to use colorants such as inorganic dyestuffs, for example, iron oxide, cobalt oxide and Prussian Blue, and organic dyestuffs, such as diazo dyestuffs or metal phthalo-cyanine dyestuffs, and trace nutritional agent, such as the salts of iron, manganese, boron, copper, cobalt, aluminum and zinc.

[0059] The active compound of the invention can be present as a mixture with other active compounds in a commercial formulation or a use form prepared from the commercial formulation. The other compounds can be insecticide, bactericide, acaricide, nematocide, fungicide, growth controller and the like. The insecticide includes, e.g., phosphates, carbamate, pyrethroids, chlorinated hydrocarbons, benzoylurea, nereistoxin and material produced by microbion such as avermectin.

[0060] Furthermore, the active compound of the invention can be present as a mixture with a synergist in a commercial formulation or a use form prepared from the commercial formulation. Synergist is used to enhance the action of active compound, as the compound itself is active it is optional to use the synergist.

[0061] Generally, the formulations contain 0.001-99.99wt%, preferably 0.01-99.9wt%, and more preferably 0.05-90wt% of the active compound of invention. The concentration of the active compound in the use form prepared from the commercial formulation can vary within a wide range. The active compound concentration of the formulation for use is, for example, 0.0000001-100 % (g/v), and preferably 0.0001- 1 %.

EXAMPLES

[0062] The invention is further illustrated by the following examples. It should be appreciated that these examples are only intended to illustrate the invention, but not to limit the scope of the invention. For the experimental methods in the following examples, they are performed under routine conditions, or as instructed by the manufacturers, unless otherwise specified. The percentage and parts are calculated by weight. Term "r.t." represents room temperature.

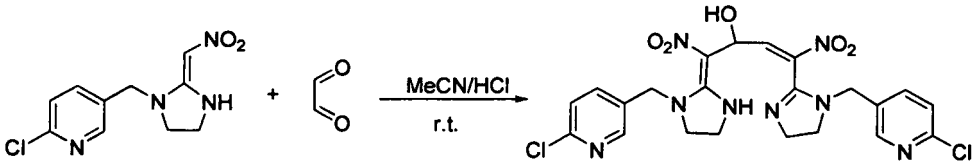
Example 1

Synthesis of 4-(1-((6-chloropyridin-3-yl)methyl)-4,5-dihydro-1H-imidazol-2-yl) -1-(1-((6-chloropyridin-3-yl)methyl)imidazolidin-2-ylidene)-1,4-dinitrobut-3-en-2-ol (compound 13)

[0063] According to the method described in WO 2006056108A1 and WO2007101369A1, 2-chloro-5-((2-(nitromethylene)imidazolidin-1-yl)methyl)pyridine was prepared from 2-chloro-5-(chloromethyl)pyridine (0.03mol) with 56% yield. Rf = 0.46 (petroleum ether: EtOAc = 1:1); mp = 156.9°C-161.8°C; GC MS(m/s): 220 (25), 126(100), 90(9).

Synthesis of 4-(1-((6-chloropyridin-3-yl)methyl)-4,5-dihydro-1H-imidazol-2-yl) -1-(1-((6-chloropyridin-3-yl)methyl)imidazolidin-2-ylidene)-1,4-dinitrobut-3-en-2-ol

[0064]

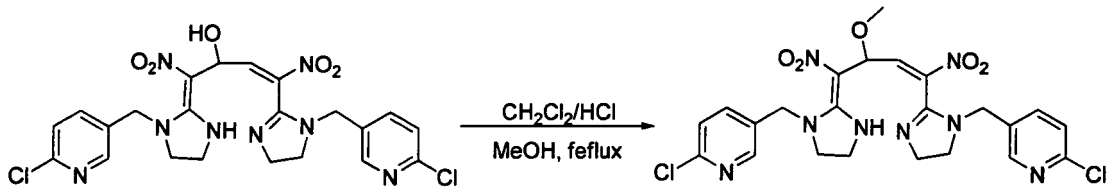


[0065] To a 50ml round bottom flask was added 1.27g (0.005mol) 2-chloro-5-((2-(nitromethylene)imidazolidin-1-yl)methyl)pyridine, 30ml acetonitrile and 3ml 30% oxaldehyde aqueous solution. After stirring for 0.5hour, catalytic concentrated HCl was added. The reaction was then stirred and monitored by TLC until completion. The mixture was filtered afterwards to afford white powder, which was crystallized to give 1.05g pure final product as white powder solid. Yield: about 76%. mp = 164.6-165.3 °C; ^{1}H NMR (400 Mz, DMSO-d_6): δ 9.01 (s, 1H), 8.41 (d, J = 2.0 Hz, 1H), 8.38 (d, J = 2.0 Hz, 1H), 7.80-7.86 (m, 2H), 7.51-7.54 (m, 2H), 6.50 (d, J = 7.2 Hz, 1H), 5.34 (d, J = 15.2 Hz, 1H), 5.18 (d, J = 15.2 Hz, 1H), 4.84 (dd, J_1 = 2.4 Hz, J_2 = 7.2 Hz, 1 H), 4.77 (d, J = 16.8 Hz, 1H), 4.67 (d, J = 16.8 Hz, 1H), 3.98 (d, J = 2.4 Hz, 1H), 3.86-3.95 (m, 2H), 3.61-3.80 (m, 5H), 3.40-3.47 (m, 1H) ppm; ^{13}C NMR (100 Mz, DMSO-d_6): δ 162.7, 158.7, 148.3, 148.2, 148.0, 147.7, 138.1, 137.7, 130.9, 130.2, 123.1, 123.0, 102.5, 101.4, 81.4, 53.8, 52.6, 49.4, 48.8, 46.4, 41.2, 41.0 ppm; HRMS (ES+) calcd for $C_{22}H_{23}N_8O_5{}^{35}Cl_2$ $(M+H)^+$, 549.1168; found, 549.1178. calcd for $C_{22}H_{23}N_8O_5{}^{35}Cl^{37}Cl$ $(M+H)^+$, 551.1139; found, 551.1152. calcd for $C_{22}H_{23}N_8O_5{}^{37}Cl_2$ $(M+H)^+$, 553.1109; found, 553.1108.

Example 2

Synthesis of 2-chloro-5-((4-(1-((6-chloropyridin-3-yl)methyl)imidazolidin-2-ylidene)-2-methoxy-1,4-dinitrobut-3-enyl)-4,5-dihydroimidazol-1-yl)methyl)pyridine (compound 14)

[0066]



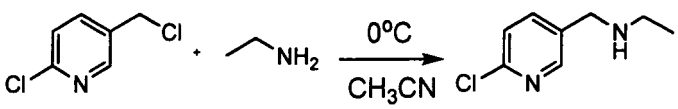
[0067] To a 50ml round bottom flask was added 0.549g (0.001mol) compound 13, 10ml methanol, 50ml dichloromethane and catalytic concentrated HCl. The reaction was refluxed and monitored by TLC. After completion, the mixture was evaporated to remove solvent and purified by column chromatography to afford final product as yellow powder (62% yield). mp = 151.6-153.1 °C; ^{1}H NMR (400 Mz, DMSO-d_6): δ 9.03 (s, 1H), 8.38 (d, J= 2.0 Hz, 1H), 8.36 (d, J = 2.0 Hz, 1H), 7.81-7.85 (m, 2H), 7.49-7.51 (m, 2H), 6.50 (d, J = 7.2 Hz, 1H), 5.35 (d, J = 15.2 Hz, 1H), 5.19 (d, J = 15.2 Hz, 1H), 4.80 (d, J_1 = 7.2 Hz, 1H), 4.77 (d, J = 16.8 Hz, 1H), 4.69 (d, J = 16.8 Hz, 1H), 3.68 (s, 3H), 3.88-3.95 (m, 2H), 3.61-3.85 (m, 5H), 3.38-3.41 (m, 1H) ppm; ^{13}C NMR (100 Mz, DMSO-d_6): δ 162.6, 158.7, 148.9, 148.3, 148.1, 147.6, 138.1, 137.8, 130.9, 129.9, 122.8, 123.1, 102.2, 101.6, 81.6, 58.7, 53.8, 52.6, 49.6, 48.9, 46.4, 41.3, 41.0 ppm; HRMS (ES+) calcd for $C_{23}H_{25}N_8O_5{}^{35}Cl_2$ $(M+H)^+$, 563.1325; found, 563.1311. calcd for $C_{23}H_{25}N_8O_5{}^{35}Cl^{37}Cl$ $(M+H)^+$, 565.1295.

Example 3

Synthesis of N^1,N^7-bis((6-chloropyridin-3-yl)methyl)-N^1,N^7-diethyl -$N^{1'}$,$N^{7'}$-dimethyl-2,6-dinitrohepta-2,5-dienediamidine (Compound 37)

(1): Synthesis of N-((6-chloropyridin-3-yl)methyl)ethanamine

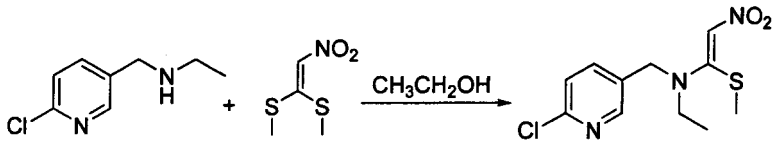
[0068]



[0069] 65-70% ethylamine solution (70 g, 1 mol), acetonitrile 50 mL were added into a three necked round bottom flask mounted with pressure-equalizing dropping funnel and thermometer. The solution was stirred in ice bath for 15min to control the temperature near 0°C. Then, 2-chloro-5-(chloromethyl)pyridine (16.10 g, 0.10 mol) in 25ml acetonitrile was added by pressure-equalizing dropping funnel in 3.5hrs with a speed of 3 drop/min. After completion, water was added and the reaction mixture was extracted with DCM. The organic phase was collected, thereby obtaining 14g N-((6-chloropyridin-3-yl)methyl)ethanamine as oil with 70% yield. GC-MS: m/z (%) = 170 ([M]+, 20), 155 (80), 126 (100), 114 (10), 90 (12).

(2): Synthesis of N-((6-chloropyridin-3-yl)methyl)-N-ethyl-1-(methylthio)-2-nitroethenamine

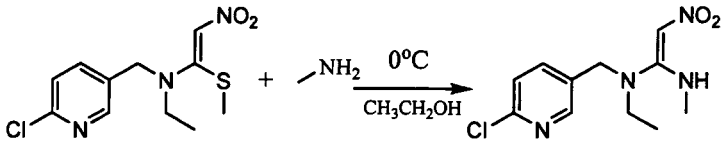
[0070]



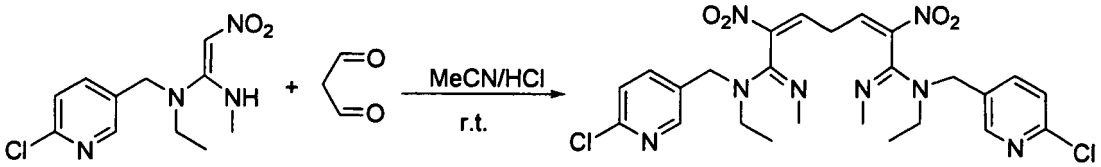
[0071] To a 100ml three necked round bottom flask was added N-((6-chloropyridin-3-yl)methyl)ethanamine (17.0 g, 0.1 mol), (2-nitroethene-1,1-diyl)bis(methylsulfane) (15.0 g, 0.09 mol), dry ethanol (50 mL). The mixture was refluxed. After completion, the reaction mixture was cooled to r.t. and concentrated under reduced pressure to obtain crude product as oil, which was purified by column chromatography to afford 5.3g N-((6-chloropyridin-3-yl)methyl)-N-ethyl-1- (methylthio)-2-nitroethenamine in 18.5% yield.
GC-MS: m/z (%) = 242 ([M]+-46, 53), 227 (15), 213 (100), 169 (45), 155 (28), 141 (29), 126 (91),90 (12).

(3): Synthesis of N-((6-chloropyridin-3-yl)methyl)-N-ethyl-N'-methyl-2 -nitroethene-1,1-diamine

[0072]



[0073] To a 100ml round bottom flask was added N-((6-chloropyridin-3-yl)methyl)-N-ethyl-1-(methylthio)-2-nitroethenamine (5 g, 0.017 mol), Methylamine alcohol solution (1.8g, 0.017 mol), dry ethanol (30 mL). The mixture was stirred in ice bath to lower the temperature to 0°C and continuously stirred until completion. The reaction mixture was evaporated under reduced pressure to remove solvent and concentrated to obtain the syrup which was solved in some DCM and purified by column chromatography using DCM/MeOH= 25:1 as eluent and silica as filler. 0.9g N-((6-chloropyridin-3-yl)methyl)-N-ethyl-N-methyl-2-nitroethene-1,1-diamine was obtained with 19.1% yield. Rf = 0.23 (DCM/Acetone = 5:1,); mp = 78-80 °C, (lit[67] 79-81 °C); GC-MS: m/z (%) =236 ([M]+-34, 32), 207 (49), 169 (52), 126 (49), 110 (20), 90 (16), 67 (100). 16.65. (4): Synthesis of N^1,N^7-bis((6-chloropyridin-3-yl)methyl)-N^1,N^7-diethyl -$N^{1'}$,$N^{7'}$-dimethyl-2,6-dinitrohepta-2,5-dienediamidine (compound 37)



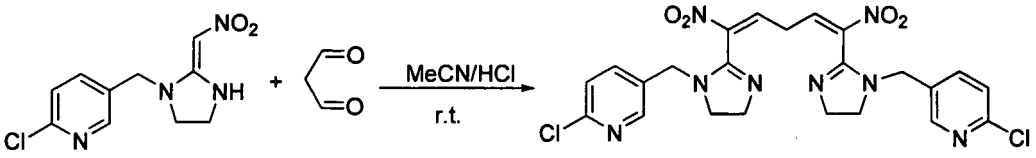
[0074] To a 50ml round bottom flask was added 1.35g (0.005mol) N-((6-chloropyridin-3-yl)methyl)-N-ethyl-N-methyl-2-nitroethene-1,1-diamine, 30ml dry acetonitrile, 0.72g (0.01mol) malonaldehyde and catalytic concentrated HCl. The reaction was stirred at r.t. and monitored by TLC. After completion, the mixture was evaporated to remove solvent and purified by column chromatography to afford final product as faint yellow powder with 56% yield.
mp = 117.3-118.7°C; ^{1}H NMR (400 Mz, DMSO-d_6): δ 8.36 (d, J= 2.4 Hz, 2H), 7.88 (dd, J_1 = 2.4 Hz, J_2 = 8.4 Hz, 2H), 7.51 (d, J = 8.4 Hz, 2H), 4.97 (t, J = 2.8 Hz, 2H), 4.86 (d, J = 15.2 Hz, 2H), 4.49 (d, J = 15.2 Hz, 2H), 3.95-3.99 (m, 4H),

3.66-3.78 (m, 6H), 3.12-3.21 (m, 2H), 1.91-1.93 (m, 6H) ppm; ^{13}C NMR (100 Mz, DMSO-d_6): δ 156.3, 148.5, 148.1, 137.3, 131.9, 122.5, 104.8, 49.2, 48.9, 48.0, 48.5, 28.1, 20.2 ppm; HRMS (EI+) calcd for $C_{25}H_{30}N_8O_4{}^{35}Cl_2$ (M^+), 576.1767; found, 576.1751.

Example 4

Synthesis of 2-chloro-5-((5-(1-((6-chloropyridin-3-yl)methyl)-4,5-dihydro -1H-imidazol-2-yl)-1,5-dinitropenta-1,4-dienyl)-4,5-dihydroimidazol-1-yl)methyl)pyridine (compound 39)

[0075]



[0076] To a 50ml round bottom flask was added 1.27g (0.005mol) 2-chloro-5-((2-(nitromethylene)imidazolidin-1-yl)methyl)pyridine, 30ml dry acetonitrile, 0.720g (0.01mol) malonaldehyde and catalytic concentrated HCl. The reaction was stirred at r.t. and monitored by TLC. After completion, the mixture was evaporated to remove solvent and purified by column chromatography to afford final product as faint yellow powder with 52% yield.
mp = 136.5-137.8 °C; ^{1}H NMR (400 Mz, DMSO-d_6): δ 8.34 (d, J= 2.4 Hz, 2H), 7.82 (dd, J_1 = 2.4 Hz, J_2 = 8.4 Hz, 2H), 7.47 (d, J = 8.4 Hz, 2H), 4.96 (t, J = 2.8 Hz, 2H), 4.81 (d, J = 15.8 Hz, 2H), 4.44 (d, J = 15.8 Hz, 2H), 3.92-3.97 (m, 4H), 3.65-3.72 (m, 2H), 3.49-3.56 (m, 2H), 1.92-1.93 (m, 2H) ppm; ^{13}C NMR (100 Mz, DMSO-d_6): δ 155.3, 147.9, 147.8, 138.0, 130.9, 122.7, 104.8, 50.2, 48.9, 48.5, 48.5, 28.1 ppm; HRMS (ES+) calcd for $C_{23}H_{23}N_8O_4{}^{35}Cl_2$ $(M+H)^+$, 545.1219; found, 545.1201. calcd for $C_{23}H_{23}N_8O_4{}^{35}Cl^{37}Cl$ $(M+H)^+$, 547.1190; found, 547.1178. calcd for $C_{23}H_{23}N_8O_4{}^{37}Cl_2$ $(M+H)^+$, 549.1160; found, 549.1181.

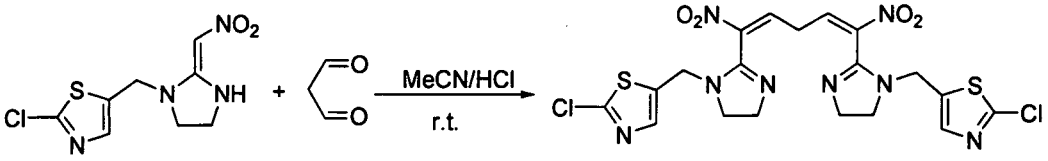
Example 5

Synthesis of 1-((2-chlorothiazol-5-yl)methyl)-5-(1-((2-chlorothiazol-5-yl)methyl) -4,5-dihydro-1H-imidazol-2-yl)-1,5-dinitropenta-1,4-dienyl)-4,5-dihydro-1H-imidazole (compound 41)

[0077] Following the method described in Example 1, 0.03mol 2-chloro-5-(chloromethyl)thiazole instead of 2-chloro-5-(chloromethyl)pyridine was used as staring material and 1-((2-chlorothiazol-5-yl)methyl)-2-(nitromethylene)imidazolidine was obtained with 56% yield. GC MS(m/s) 226(24), 132(100), 77(9).

Synthesis of 1-((2-chlorothiazol-5-yl)methyl)-5-(1-((2-chlorothiazol-5-yl) methyl)-4,5-dihydro-1H-imidazol-2-yl)-1,5-dinitropenta-1,4-dienyl)-4,5-dihydro-1H-imidazole

[0078]



[0079] To a 50ml round bottom flask was added 1.30g (0.005mol) 1-((2-chlorothiazol-5-yl)methyl)-2-(nitromethylene)imidazolidine, 30ml dry acetonitrile, 0.720g (0.01mol) malonaldehyde and catalytic concentrated HCl. The reaction was stirred at r.t. and monitored by TLC. After completion, the mixture was evaporated to remove solvent and purified by column chromatography to afford final product as faint yellow powder with 44% yield.
mp = 138.6-139.9 °C; ^{1}H NMR (400 Mz, DMSO-d_6): δ 7.63 (s, 1H), 4.98 (t, J= 2.8 Hz, 2H), 4.85 (d, J = 15.8 Hz, 2H), 4.43 (d, J = 15.8 Hz, 2H), 3.96-3.99 (m, 4H), 3.67-3.71 (m, 2H), 3.51-3.56 (m, 2H), 1.95-1.97 (m, 2H) ppm; ^{13}C NMR (100 Mz, DMSO-d_6): δ 157.6, 149.3, 138.3, 105.8, 50.6, 48.9, 48.4, 48.1, 29.1 ppm; HRMS (ES+) calcd for $C_{19}H_{19}N_8O_4S_2{}^{35}Cl_2$ $(M+H)^+$, 557.0348; found, 557.0363. calcd for $C_{19}H_{19}N_8O_4S_2{}^{35}Cl^{37}Cl$ $(M+H)^+$, 559.0318; found, 559.0620.

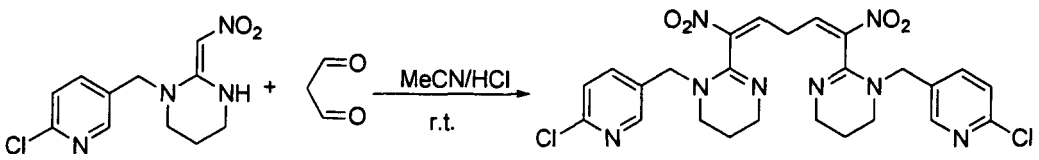
Example 6

Synthesis of 1-((6-chloropyridin-3-yl)methyl)-5-(1-((6-chloropyridin-3-yl) methyl)-1,4,5,6-tetrahydropyrimidin-2-yl)-1,5-dinitropenta-1,4-dienyl)-1,4,5,6-tetrahydropyrim idine (compound 43)

[0080] According to the method described in WO 2006056108A1 and WO2007101369A1, 1-((6-chloropyridin-3-yl)methyl)-2-(nitromethylene)-hexahydropyrimidine was prepared from 2.42g (0.015 mmol) 2-chloro-5-(chloromethyl)pyridine with 56% yield; R_f= 0.19 (EtOH: DCM = 1:1); mp = 175.7°C-182.6°C; GC MS(m/s): 225(100), 196(9), 154(10), 139(11), 126(31), 113(10),90(31).

Synthesis of 1-((6-chloropyridin-3-yl)methyl)-5-(1-((6-chloropyridin-3-yl) methyl)-1,4,5,6-tetrahydropyrimidin-2-yl)-1,5-dinitropenta-1,4-dienyl)-1,4,5,6-tetrahydropyrim idine

[0081]

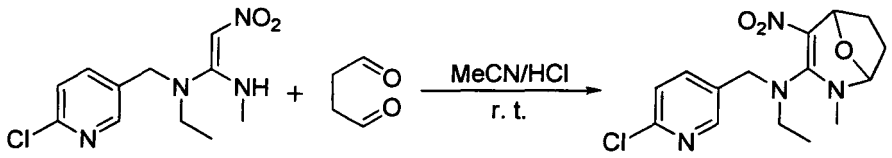


[0082] To a 50ml round bottom flask was added 1.34g (0.005mol) 1-((6-chloropyridin-3-yl)methyl)-2-(nitromethylene)-hexahydropyrimidine, 30ml dry acetonitrile and 0.720g (0.01mol) malonaldehyde and catalytic concentrated HCl. The reaction was stirred at r.t. and monitored by TLC. After completion, the mixture was evaporated to remove solvent and purified by column chromatography to afford final product as faint yellow powder with 55% yield.
mp = 133.7-134.9 °C; ^{1}H NMR (400 Mz, DMSO-d_6): δ 8.32 (d, J= 2.4 Hz, 2H), 7.81 (dd, J_1 = 2.4 Hz, J_2 = 8.4 Hz, 2H), 7.49 (d, J = 8.4 Hz, 2H), 4.93 (t, J= 2.8 Hz, 2H), 4.78 (d, J = 15.8 Hz, 2H), 4.40 (d, J = 15.8 Hz, 2H), 3.91-3.96 (m, 4H), 3.63-3.71 (m, 2H), 3.49-3.53 (m, 2H), 2.32-2.37 (m, 2H), 1.92-1.93 (m, 2H) ppm; ^{13}C NMR (100 Mz, DMSO-d_6): δ 155.6, 148.3, 147.9, 138.0, 130.7, 122.7, 105.1, 50.2, 48.8, 48.5, 48.1, 36.2, 28.0 ppm; HRMS (ES+) calcd for $C_{25}H_{27}N_8O_4{}^{35}Cl_2$ $(M+H)^+$, 572.1454; found, 572.1468. calcd for $C_{25}H_{27}N_8O_4{}^{35}Cl^{37}Cl$ $(M+H)^+$, 574.1425; found, 574.1416.

Example 7

Synthesis of N-((6-chloropyridin-3-yl)methyl)-N-ethyl-2-methyl-4-nitro-8-oxa-2 -aza-bicyclo[3.2.1]oct-3-en-3-amine (compound 46)

[0083]

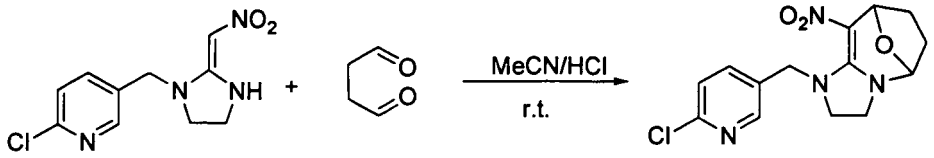


[0084] To a 50ml round bottom flask was added 1.35g (0.005mol) N-((6-chloropyridin-3-yl)methyl)-N-ethyl-N'-methyl-2-nitroethene-1,1-diamine, 30ml dry acetonitrile, 0.860g (0.01mol) succinaldehyde and catalytic concentrated HCl. The reaction was stirred at r.t. and monitored by TLC. After completion, the mixture was evaporated to remove solvent and purified by column chromatography to afford final product as faint yellow powder with 40% yield.
mp = 125.3-125.7°C; ^{1}H NMR (400 Mz, DMSO-d_6): δ 8.72 (s, 1H), 8.27 (d, J= 2.4 Hz, 1H), 7.75 (dd, J_1 = 2.4 Hz, J_2 = 8.4 Hz, 1H), 7.58 (d, J = 8.4 Hz, 1H), 5.25-5.30 (s, 2H), 4.41-4.50 (m, 2H), 2.96-3.26 (m, 2H), 2.86 (s, 3H), 2.36-2.41 (m, 2H), 1.81-1.5 (m, 4H), 1.16-1.26 (m, 3H) ppm; ^{13}C NMR (100 Mz, DMSO-d6): δ 158.5, 154.4, 151.6, 150.8, 148.1, 139.3, 137.1, 107.8, 89.5, 65.8, 49.8, 46.9, 40.6, 21.9, 20.3 ppm; HRMS (EI+) calcd for $C_{15}H_{21}N_4O_3{}^{35}Cl$ (M^+), 339.1224; found, 339.1257. calcd for $C_{15}H_{21}N_4O_3{}^{37}Cl$ (M^+), 341.1194; found, 341.1213.

Example 8

Synthesis of 1-((6-chloropyridin-3-yl)methyl)-9-nitro-2,3,5,6,7,8-hexahydro-1H-5,8-epoxyimidazo[1,2-a]azepine (compound 52)

[0085]

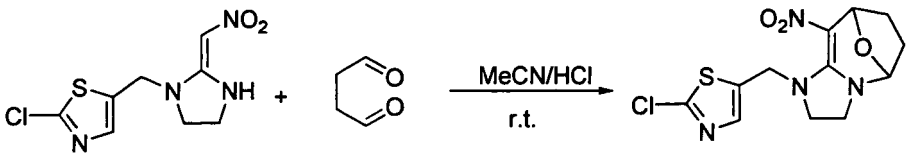


[0086] To a 50ml round bottom flask was added 1.27g (0.005mol) 2-chloro-5-((2-(nitromethylene)imidazolidin-1-yl)methyl)pyridine, 30ml dry acetonitrile, 0.860g (0.01mol) succinaldehyde and catalytic concentrated HCl. The reaction was stirred at r.t. and monitored by TLC. After completion, the mixture was evaporated to remove solvent and purified by column chromatography to afford final product as faint yellow powder with 71% yield.
mp = 149.0-150.0 °C; ^{1}H NMR (400 Mz, DMSO-d_6): δ 8.35 (d, J= 2.4 Hz, 1H), 7.81 (dd, J_1 = 2.4 Hz, J_2 = 8.4 Hz, 1H), 7.51 (d, J = 8.4 Hz, 1H), 5.36-5.39 (s, 2H), 5.00 (d, J = 15.6 Hz, 1H), 4.68 (d, J = 15.6 Hz, 1H), 3.57-3.73 (m, 4H), 1.94-2.04 (m, 4H) ppm; ^{13}C NMR (100 Mz, DMSO-d_6): δ 155.6, 149.7, 149.6, 139.7, 132.6, 124.5, 109.6, 87.0, 75.1, 51.2, 50.3, 46.6, 31.9, 31.7 ppm; HRMS (ES+) calcd for $C_{14}H_{16}N_4O_3{}^{35}Cl$ $(M+H)^+$, 323.0911; found, 323.0912. calcd for $C_{14}H_{16}N_4O_3{}^{37}Cl$ $(M+H)^+$, 325.0811; found, 325.0895. calcd for $C_{14}H_{15}N_4O_3{}^{35}ClNa$ $(M+Na)^+$, 345.0730; found, 345.0722. calcd for $C_{14}H_5N_4O_3{}^{37}ClNa$ $(M+Na)^{++}$, 347.0701; found, 347.0692.

Example 9

Synthesis of 1-((2-chlorothiazol-5-yl)methyl)-9-nitro-2,3,5,6,7,8-hexahydro -1H-5,8-epoxyimidazo[1,2-a]azepine (compound 53)

[0087]

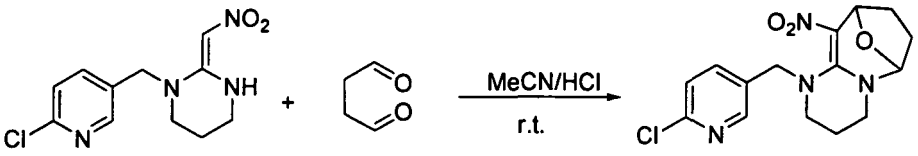


[0088] To a 50ml round bottom flask was added 1.30g (0.005mol) 1-((2-chlorothiazol-5-yl)methyl)-2-(nitromethylene)imidazolidine, 30ml dry acetonitrile, 0.860g (0.01mol) succinaldehyde and catalytic concentrated HCl. The reaction was stirred at r.t. and monitored by TLC. After completion, the mixture was evaporated to remove solvent and purified by column chromatography to afford final product as faint yellow powder with 63% yield.
mp = 151.7-152.1 °C; ^{1}H NMR (400 Mz, DMSO-d_6): δ 7.65 (s, 1H), 5.33-5.37 (s, 2H), 5.01 (d, J = 15.6 Hz, 1H), 4.69 (d, J = 15.6 Hz, 1H), 3.52-3.70 (m, 4H), 1.90-2.01 (m, 4H) ppm; ^{13}C NMR (100 Mz, DMSO-d_6): δ 155.2, 149.6, 139.1, 124.5, 110.6, 87.1, 75.6, 51.3, 50.6, 46.9, 31.9, 31.2 ppm; HRMS (ES+) calcd for $C_{12}H_{15}N_4O_3S^{35}Cl$ $(M+H)^+$, 329.0475; found, 329.0412. calcd for $C_{12}H_{15}N_4O_3S^{37}Cl$ $(M+H)^+$, 331.0446; found, 331.0423.

Example 10

Synthesis of 1-((6-chloropyridin-3-yl)methyl)-10-nitro-1,2,3,4,6,7,8,9-octahydro -6,9-epoxypyrimido[1,2-a]azepine (compound 61)

[0089]

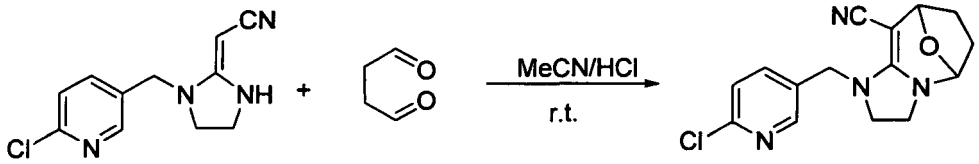


[0090] To a 50ml round bottom flask was added 1.34g (0.005mol) (E)-1-((6-chloropyridin-3-yl)methyl)-2-(nitromethylene)-hexahydropyrimidine, 30ml dry acetonitrile and 0.860g (0.01mol) succinaldehyde and catalytic concentrated HCl. The reaction was stirred at r.t. and monitored by TLC. After completion, the mixture was evaporated to remove solvent and purified by column chromatography to afford final product as faint yellow powder with 38% yield.
mp = 143.2-144.9 °C; ^{1}H NMR (400 Mz, DMSO-d_6): δ 8.33 (d, J= 2.4 Hz, 1H), 7.80 (dd, J_1 = 2.4 Hz, J_2 = 8.4 Hz, 1H), 7.49 (d, J = 8.4 Hz, 1H), 5.32-5.35 (s, 2H), 5.00 (d, J = 15.6 Hz, 1H), 4.66 (d, J = 15.6 Hz, 1H), 3.51-3.68 (m, 4H), 2.33-2.41 (m, 2H), 1.89-2.00 (m, 4H) ppm; ^{13}C NMR (100 Mz, DMSO-d_6): δ 155.5, 149.6, 149.3, 139.7, 132.6, 124.1, 109.3, 86.6, 75.1, 51.2, 50.7, 46.6, 32.1, 31.7, 26.9 ppm; HRMS (ES+) calcd for $C_{15}H_{19}N_4O_3{}^{35}Cl$ $(M+H)^+$, 337.1067; found, 337.1015. calcd for $C_{15}H_{19}N_4O_3{}^{37}Cl$ $(M+H)^+$, 339.1038; found, 339.0995.

Example 11

Synthesis of 1-((6-chloropyridin-3-yl)methyl)-2,3,5,6,7,8-hexahydro-1H-5,8-epoxyimidazo[1,2-a]azepine-9-carbonitrile (compound 64)

[0091]

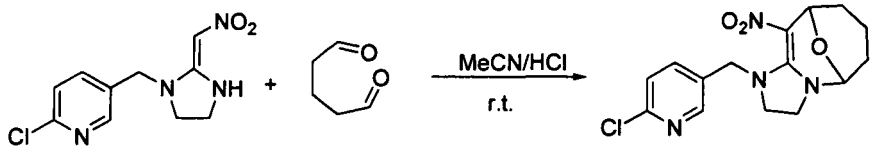


[0092] To a 50ml round bottom flask was added 1.17g (0.005mol) 2-(1-((6-chloropyridin-3-yl)methyl)imidazolidin-2-ylidene)acetonitrile, 30ml dry acetonitrile and 0.860g (0.01mol) succinaldehyde and catalytic concentrated HCl. The reaction was stirred at r.t. and monitored by TLC. After completion, the mixture was evaporated to remove solvent and purified by column chromatography to afford final product as faint yellow powder with 66% yield.
mp = 125.1-126.8 °C; ^{1}H NMR (400 Mz, DMSO-d_6): δ 8.34 (d, J= 2.4 Hz, 1H), 7.82 (dd, J_1 = 2.4 Hz, J_2 = 8.4 Hz, 1H), 7.55 (d, J = 8.4 Hz, 1H), 5.33 (s, 1H), 5.25 (s, 1H), 5.00 (d, J = 15.6 Hz, 1H), 4.78 (d, J = 15.6 Hz, 1H), 3.56-3.78 (m, 4H), 1.91-2.00 (m, 4H) ppm; ^{13}C NMR (100 Mz, DMSO-d_6): δ 153.6, 149.0, 148.6, 139.7, 132.3, 121.5, 99.6, 87.3, 75.7, 51.3, 50.2, 46.6, 31.5, 29.7 ppm; HRMS (ES+) calcd for $C_{15}H_{16}N_4O^{35}Cl$ $(M+H)^+$, 303.1013; found, 303.0992. calcd for $C_{15}H_{16}N_4O^{37}Cl$ $(M+H)^+$, 305.0983; found, 305.0957.

Example 12

Synthesis of 1-((6-chloropyridin-3-yl)methyl)-10-nitro-1,2,3,5,6,7,8,9-octahydro-5,9-epoxyimidazo[1,2-a]azocine (compound 77)

[0093]



[0094] To a 50ml round bottom flask was added 1.27g (0.005mol) 2-chloro-5-((2-(nitromethylene)imidazolidin-1-yl)methyl)pyridine, 30ml acetonitrile, 3ml 25% glutaraldehyde aqueous solution and catalytic concentrated HCl. The reaction was stirred at r.t. and monitored by TLC. After completion, the mixture was evaporated to remove solvent and purified by column chromatography to afford final product as faint yellow powder with 86% yield.
mp = 174.7-175.4 °C; ^{1}H NMR (400 Mz, DMSO-d_6): δ 8.38 (dd, J_1 = 0.6 Hz, J_2 = 2.4 Hz, 1H), 7.84 (dd, J_1 = 2.4 Hz, J_2

= 8.4 Hz, 1H), 7.52 (dd, J_1 = 0.6 Hz, J_2 = 8.4 Hz, 1H), 5.12 (s, 1H), 5.04-5.05 (m, 1H), 4.97 (d, J = 15.6 Hz, 1H), 4.71 (d, J = 15.6 Hz, 1H), 3.62-3.74 (m, 4H), 1.66-1.81 (m, 4H), 1.51-1.55 (m, 1H), 1.32-1.44 (m, 1H) ppm; ^{13}C NMR (100 Mz, DMSO-d_6): δ 156.6, 149.7, 149.6, 139.7, 132.9, 124.5, 105.8, 81.7, 68.9, 51.7, 50.0, 46.3, 28.8, 27.2, 14.8 ppm; HRMS (EI+) calcd for $C_{15}H_{17}N_4O_3{}^{35}Cl$ (M^+), 336.0989; found, 336.0988. calcd for $C_{15}H_{17}N4O_3{}^{37}Cl$ (M^+), 338.0960; found, 338.0968.

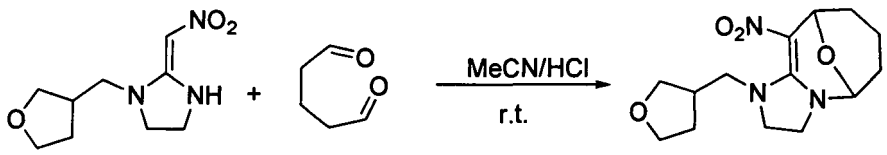
Example 13

Synthesis of 10-nitro-1-((tetrahydrofuran-3-yl)methyl)-1,2,3,5,6,7,8,9-octahydro-5,9-epoxyimidazo[1,2-a]azocine (compound 80)

[0095] Following the method described in Example 1, 0.2 mol 3-(chloromethyl)tetrahydrofuran instead of 2-chloro-5-(chloromethyl)pyridine was used as staring material. 2-(nitromethylene)-1-((tetrahydrofuran-3-yl)methyl)imidazolidine was obtained with 51% yield. GC MS(m/s) 177(29), 99(100), 56(9).

Synthesis of 10-nitro-1-((tetrahydrofuran-3-yl)methyl)-1,2,3,5,6,7,8,9-octahydro -5,9-epoxyimidazo[1,2-a]azocine

[0096]



[0097] To a 50ml round bottom flask was added 1.065g (0.005mol) 2-(nitromethylene)-1-((tetrahydrofuran-3-yl)methyl)imidazolidine, 30ml acetonitrile, 3ml 25% glutaraldehyde aqueous solution and catalytic concentrated HCl. The reaction was stirred at r.t. and monitored by TLC. After completion, the mixture was evaporated to remove solvent and purified by column chromatography to afford final product as yellow powder with 36% yield.
mp = 115.3-116.9°C; ^{1}H NMR (400 Mz, DMSO-d_6): δ 5.11 (s, 1H), 5.00-5.03 (m, 1H), 4.18 (d, J = 3.2 Hz, 2H), 4.05-4.25 (m, 2H), 3.85-3.96 (m, 4H), 2.25 (m, 1H), 1.66-1.81 (m, 4H), 1.63 -1.64 (m, 2H), 1.57-1.59 (m, 2H), 1.51-1.55 (m, 1H), 1.32-1.44 (m, 1H) ppm; ^{13}C NMR (100 Mz, DMSO-d_6): δ 81.7, 80.6, 78.5, 68.9, 50.0, 49.7, 46.9, 44.6, 36.8, 33.9, 28.8, 27.2, 17.8, 14.8ppm; HRMS (EI+) calcd for $C_{14}H_{21}N_3O_4$ (M^+), 295.1532; found, 295.1598.

Example 14

Insecticidal Activity Test of the invented compounds

(1) Activity Test for Cowpea Aphids (*Aphis craccivoral*)

[0098] Aphis, which belongs to Homoptera and has a piercing-sucking mouthpart, is a common insect for agricultural plant. *Aphis craccivoral* was tested by the way of immersing.

[0099] Test method: exactly weighed various samples were independently added to N,N-dimethylformamide to form a 10g/L stock solution. The mixture was diluted with 0.2mL/L aqueous Triton X-100 solution to a concentration of 500ppm After stably sucking on bean sprout, the adult aphis without wings together with bean sprout was dipped into 500ppm dilution, taken out after 5 seconds, and the excess dilution was sucked out with bibulous paper and the adult aphis without wings was incubated in clean vessel at a constant temperature of 23 °C. Each concentration was repeated for 3 times and the control group contained 0.2mL/L aqueous Triton X-100 solution. The number of killed aphis was counted after 24 hours to calculate the mortality by the following formula:

$$\text{mortality}(\%) = (\text{control alive aphis- treated alive aphis})/\text{control alive aphis} \times 100\%.$$

[0100] The results were shown in Tables 1-4 bellow.

(2) Activity Test for Planthopper (*Nilaparvata lugens*)

[0101] Planthopper, which belongs to Homoptera and has a piercing-sucking mouthpart, is a common insect for agricultural plant. *Nilaparvata lugens* was tested by the way of spraying.

[0102] Test method: the test compound was exactly formulated into a solution of acetone to final concentration of 500, 250, 100, 50, 25, 12.5, 6.25, 3.13, 1.57 and 0.79 ppm. The acetone aqueous solution was used as control. Each process was repeated for 3 tumblers (3 times). 2mL of solution was sprayed uniformly to each cup by a mini manual sprayer. 10 *Nilaparvata lugens* were introduced to every sink 6 hours before spraying. Three series of experiments were conducted. The number of killed *Nilaparvata lugens* was counted after 24 hours to calculate the mortality using above mentioned formula. The results were shown in Tables 1-4 bellow.

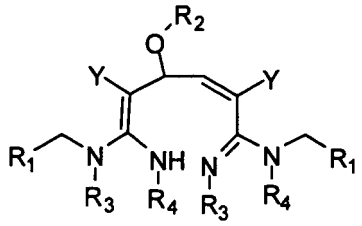
(3) Activity Test for Armyworm (*Pseudaletia separate Walker*)

[0103] Armyworm was tested by the way of feeding immersed leaves. The test compound was exactly formulated into a solution of acetone to concentration 500, 250, 100, 50, 25, 12.5, 6.25, 3.13 and 1.57 ppm. The acetone aqueous solution was used as control. Fresh maize leaves were immersed in the solution for 3 seconds and dried at room temperature and used to feed the tested insects. Each process was repeated for 3 times while 10 Armyworms were tested in each experiment. The number of killed Armyworms was counted after 24 hours to calculate the mortality using above mentioned formula. The results were shown in Tables 1-4 bellow.

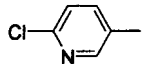
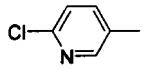
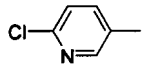
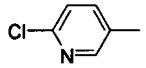
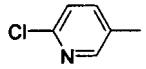
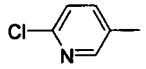
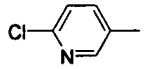
(4) Activity Test for Diamondback moth *(Plutella xylostella)*

[0104] Diamondback moth was tested by the way of feeding immersed leaves. Fresh cabbage leaves were immersed in above mentioned solution for 3 seconds and dried at room temperature and used to feed to the tested insects. Each process was repeated for 3 tumblers (3 times) while 10 Diamondback moths were tested in each experiment, while water was used as control. The number of killed Diamondback moth was counted after 24 hours to calculate the mortality using above mentioned formula. The results were shown in Tables 1-4 bellow.

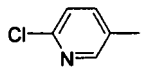
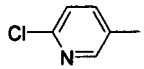
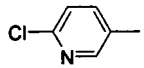
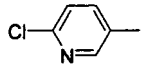
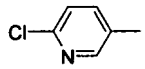
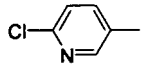
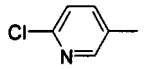
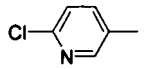
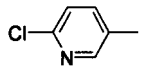
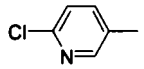
Table 1 Insecticidal Activities of Compound of formula (A)



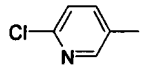
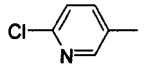
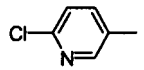
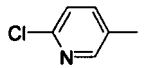
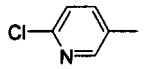
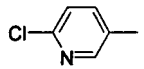
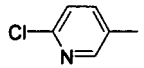
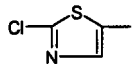
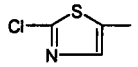
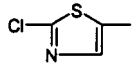
(A)

Compd. No.	R_1	R_2	R_3	R_4	Y	Insecticidal Activity			
						Cowpea Aphids	Planth-opper	Army-worm	Diamo-nd back moth
						Mortality (100%) 500ppm	Mortality (100%) 500ppm	Mortality (100%) 500ppm	Mortality (100%) 500ppm
1		H	C_2H_5	CH_3	NO_2	80	91	100	100
2		CH_3	C_2H_5	CH_3	NO_2	100	100	100	100
3		C_2H_5	C_2H_5	CH_3	NO_2	100	100	100	100
4		C_3H_7	C_2H_5	CH_3	NO_2	100	100	100	100
5		*i*-C_3H_7	C_2H_5	CH_3	NO_2	100	100	100	100
6		benzyl	C_2H_5	CH_3	NO_2	100	100	100	100
7		H	H	CH_3	NO_2	24	35	35	21

(continued)

Compd. No.	R_1	R_2	R_3	R_4	Y	Insecticidal Activity			
						Cowpea Aphids	Planth-opper	Army-worm	Diamo-nd back moth
						Mortality (100%) 500ppm	Mortality (100%) 500ppm	Mortality (100%) 500ppm	Mortality (100%) 500ppm
8		CH_3	H	CH_3	NO_2	45	44	67	56
9		C_2H_5	H	CH_3	NO_2	89	87	100	100
10		C_3H_7	H	CH_3	NO_2	45	36	87	90
11		i-C_3H_7	H	CH_3	NO_2	76	90	95	100
12		benzyl	H	CH_3	NO_2	67	92	97	100
13		H	R_3 and R_4 together form $-CH_2-CH_2-$		NO_2	78	85	100	100
14		CH_3	R_3 and R_4 together form $-CH_2-CH_2-$		NO_2	100	100	100	100
15		C_2H_5	R_3 and R_4 together form $-CH_2-CH_2-$		NO_2	100	100	100	100
16		C_3H_7	R_3 and R_4 together form $-CH_2-CH_2-$		NO_2	100	100	100	100
17		i-C_3H_7	R_3 and R_4 together form $-CH_2-CH_2-$		NO_2	100	100	100	100

(continued)

Compd. No.	R_1	R_2	R_3	R_4	Y	Insecticidal Activity			
						Cowpea Aphids	Planth-opper	Army-worm	Diamo-nd back moth
						Mortality (100%) 500ppm	Mortality (100%) 500ppm	Mortality (100%) 500ppm	Mortality (100%) 500ppm
18		benzyl	R_3 and R_4 together form $-CH_2-CH_2-$		NO_2	100	100	100	100
19		H	R_3 and R_4 together form $-CH_2-CH_2-$		CN	90	100	100	100
20		H	R_3 and R_4 together form $-CH_2-CH_2-$		CN	98	100	100	100
21		H	R_3 and R_4 together form $-CH_2-CH_2-$		CN	100	100	100	100
22		H	R_3 and R_4 together form $-CH_2-CH_2-$		CN	73	100	92	100
23		H	R_3 and R_4 together form $-CH_2-CH_2-$		CN	56	87	87	100
24		H	R_3 and R_4 together form $-CH_2-CH_2-$		CN	65	83	90	100
25		H	R_3 and R_4 together form $-CH_2-CH_2-$		NO_2	89	87	100	100
26		H	R_3 and R_4 together form $-CH_2-CH_2-$		NO_2	100	100	100	100
27		H	R_3 and R_4 together form $-CH_2-CH_2-$		NO_2	100	100	100	100

(continued)

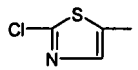
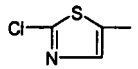
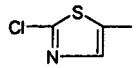
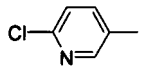
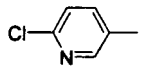
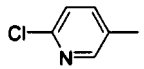
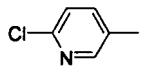
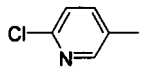
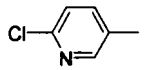
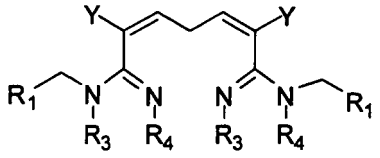
Compd. No.	R_1	R_2	R_3	R_4	Y	Insecticidal Activity			
						Cowpea Aphids	Planth-opper	Army-worm	Diamo-nd back moth
						Mortality (100%) 500ppm	Mortality (100%) 500ppm	Mortality (100%) 500ppm	Mortality (100%) 500ppm
28		H	R_3 and R_4 together form $-CH_2-CH_2-$		NO_2	100	100	100	100
29		H	R_3 and R_4 together form $-CH_2-CH_2-$		NO_2	100	100	100	100
30		H	R_3 and R_4 together form $-CH_2-CH_2-CH_2$		NO_2	100	100	100	100
31		H	R_3 and R_4 together form $-CH_2-CH_2-CH_2$		NO_2	46	77	77	83
32		H	R_3 and R_4 together form $-CH_2-CH_2-CH_2$		NO_2	65	61	87	92
33		H	R_3 and R_4 together form $-CH_2-CH_2-CH_2$		NO_2	32	50	58	52
34		H	R_3 and R_4 together form $-CH_2-CH_2-CH_2$		NO_2	76	88	90	86
35		H	R_3 and R_4 together form $-CH_2-CH_2-CH_2$		NO_2	76	90	68	77
36		H	R_3 and R_4 together form $-CH_2-CH_2-CH_2$		NO_2	87	97	100	100

Table 2 Insecticidal Activities of Compound of formula (B)



(B)

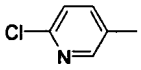
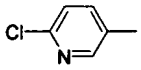
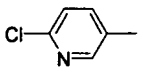
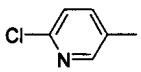
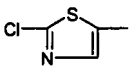
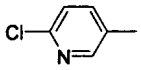
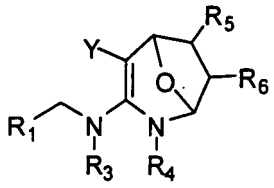
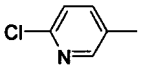
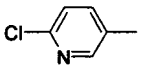
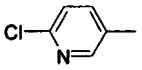
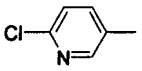
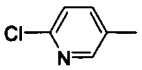
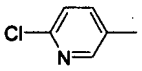
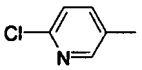
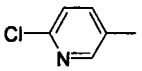
Compd. No.	R_1	R_3	R_4	Y	Insecticidal Activity			
					Cowpea Aphids	Planth-opper	Army-worm	Diamo-ndb ack moth
					Mortality (100%) 500ppm	Mortality (100%) 500ppm	Mortality (100%) 500ppm	Mortality (100%) 500ppm
37		C_2H_5	CH_3	NO_2	100	100	100	100
38		H	CH_3	NO_2	100	100	100	100
39		R_3 and R_4 together form $-CH_2-CH_2-$		NO_2	100	100	100	100
40		R_3 and R_4 together form $-CH_2-CH_2-$		CN	56	87	87	100
41		R_3 and R_4 together form $-CH_2-CH_2-$		NO_2	100	100	100	100
42		R_3 and R_4 together form $-CH_2-CH_2-$		NO_2	100	100	100	100
43		R_3 and R_4 together form $-CH_2-CH_2-CH_2-$		NO_2	78	87	100	96

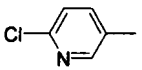
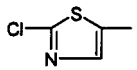
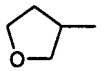
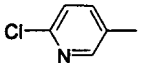
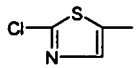
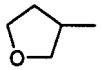
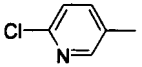
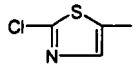
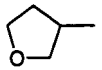
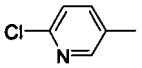
Table 3 Insecticidal Activities of Compound of formula (C)



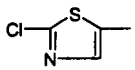
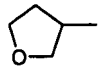
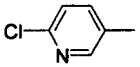
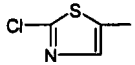
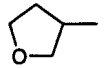
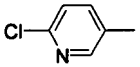
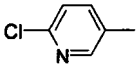
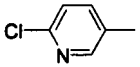
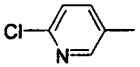
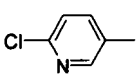
(C)

Compd. No.	R_1	R_3	R_4	R_5	R_6	Y	Insecticidal Activity			
							Cowpea Aphids	Planth-opper	Army-worm	Diamo-nd back moth
							Mortality (100%) 500ppm	Mortality (100%) 500ppm	Mortality (100%) 500ppm	Mortality (100%) 500ppm
44		H	CH_3	H	H	NO_2	100	100	100	100
45		CH_3	CH_3	H	H	NO_2	100	100	100	100
46		C_2H_5	CH_3	H	H	NO_2	100	100	100	100
47		H	H	H	H	NO_2	100	100	100	100
48		CH_3	H	H	H	NO_2	100	100	100	100
49		C_2H_5	H	H	H	NO_2	100	100	100	100
50		CH_3	C_2H_5	H	H	NO_2	100	100	100	100
51		C_2H_5	C_2H_5	H	H	NO_2	100	100	100	100

(continued)

Compd. No.	R_1	R_3	R_4	R_5	R_6	Y	Insecticidal Activity			
							Cowpea Aphids	Planth-opper	Army-worm	Diamo-nd back moth
							Mortality (100%) 500ppm	Mortality (100%) 500ppm	Mortality (100%) 500ppm	Mortality (100%) 500ppm
52		R_3 and R_4 together form $-CH_2-CH_2-$		H	H	NO_2	100	100	100	100
53		R_3 and R_4 together form $-CH_2-CH_2-$		H	H	NO_2	100	100	100	100
54		R_3 and R_4 together form $-CH_2-CH_2-$		H	H	NO_2	100	100	100	100
55		R_3 and R_4 together form $-CH_2-CH_2-$		CH_3	CH_3	NO_2	100	100	100	100
56		R_3 and R_4 together form $-CH_2-CH_2-$		CH_3	CH_3	NO_2	100	100	100	100
57		R_3 and R_4 together form $-CH_2-CH_2-$		CH_3	CH_3	NO_2	100	100	100	100
58		R_3 and R_4 together form $-CH_2-CH_2-$		F	F	NO_2	100	100	100	100
59		R_3 and R_4 together form $-CH_2-CH_2-$		F	F	NO_2	100	100	100	100
60		R_3 and R_4 together form $-CH_2-CH_2-$		F	F	NO_2	100	100	100	100
61		R_3 and R_4 together form $-CH_2-CH_2-CH_2-$		H	H	NO_2	65	75	76	35

(continued)

Compd. No.	R_1	R_3	R_4	R_5	R_6	Y	Insecticidal Activity			
							Cowpea Aphids	Planth-opper	Army-worm	Diamo-nd back moth
							Mortality (100%) 500ppm	Mortality (100%) 500ppm	Mortality (100%) 500ppm	Mortality (100%) 500ppm
62		R_3 and R_4 together form $-CH_2-CH_2-CH_2-$		H	H	NO_2	75	50	89	33
63		R_3 and R_4 together form $-CH_2-CH_2-CH_2-$		H	H	NO_2	37	76	53	87
64		R_3 and R_4 together form $-CH_2-CH_2-$		H	H	CN	96	56	100	100
65		R_3 and R_4 together form $-CH_2-CH_2-$		H	H	CN	80	86	98	100
66		R_3 and R_4 together form $-CH_2-CH_2-$		H	H	CN	37	44	50	41
67		R_3 and R_4 together form $-CH_2-CH_2-$		H	CH_3O	NO_2	100	100	100	100
68		R_3 and R_4 together form $-CH_2-CH_2-$		H	C_2H_5O	NO_2	100	100	100	100
69		R_3 and R_4 together form $-CH_2-CH_2-$		CH_3O	H	NO_2	100	100	100	100
70		R_3 and R_4 together form $-CH_2-CH_2-$		C_2H_5O	H	NO_2	100	100	100	100
71		R_3 and R_4 together form $-CH_2-CH_2-$			H	NO_2	100	100	100	100

(continued)

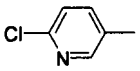
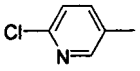
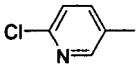
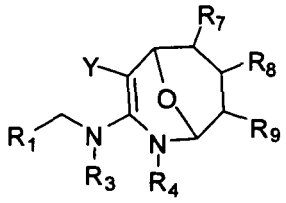
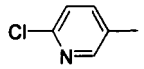
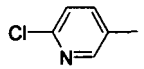
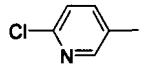
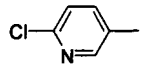
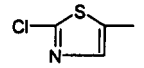
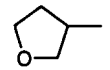
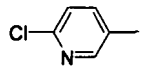
Compd. No.	R_1	R_3	R_4	R_5	R_6	Y	Insecticidal Activity			
							Cowpea Aphids	Planth-opper	Army-worm	Diamo-nd back moth
							Mortality (100%) 500ppm	Mortality (100%) 500ppm	Mortality (100%) 500ppm	Mortality (100%) 500ppm
72		R_3 and R_4 together form $-CH_2-CH_2-$			H	NO_2	100	100	100	100
73		R_3 and R_4 together form $-CH_2-CH_2-$		H		NO_2	100	100	100	100
74		R_3 and R_4 together form $-CH_2-CH_2-$		H		NO_2	100	100	100	100

Table 4 Insecticidal Activities of Compound of formula (D)



(D)

Compd. No.	R_1	R_3	R_4	R_7, R_8, R_9	Y	Insecticidal Activitv			
						Cowpea Aphids	Planth-opper	Army-worm	Diamo-nd back moth
						Mortality (100%) 500ppm	Mortality (100%) 500ppm	Mortality (100%) 500ppm	Mortality (100%) 500ppm
75		C_2H_5	CH_3	H	NO_2	100	100	100	100
76		H	CH_3	H	NO_2	100	100	100	100
77		R_3 and R_4 together form $-CH_2-CH_2-$		H	NO_2	100	100	100	100
78		R_3 and R_4 together form $-CH_2-CH_2-$		H	CN	56	87	87	100
79		R_3 and R_4 together form $-CH_2-CH_2-$		H	NO_2	100	100	100	100
80		R_3 and R_4 together form $-CH_2-CH_2-$		H	NO_2	100	100	100	100
81		R_3 and R_4 together form $-CH_2-CH_2-CH_2$		H	NO_2	78	87	100	96

Example 15

Preparation of insecticidal composition containing the invented active compound

(a) Oily Suspension

[0105] The following components were prepared: 25 wt% of any compound selected from compounds 1-73; 5 wt% polyoxyethylene sorbital hexaoleate and 70 wt% higher aliphatic hydrocarbon oil. All of the components were ground in a sand mill until the solid granules were reduced to less than about 5 micrometer. The resultant viscous suspension could be used directly or may be used after it was emulsified in water.

(b) Aqueous Suspension

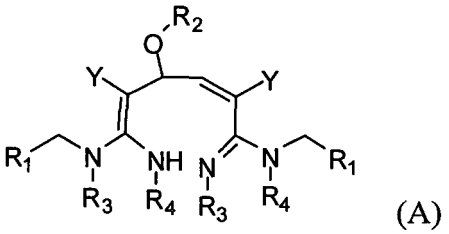
[0106] The following components were prepared: 25 wt% of any compound selected from compounds 1-73; 3 wt% hydrate attapulagit; 10 wt% calcium lignosulphonate; 0.5 wt% sodium dihydrogen phosphate and 61.5 wt% water. All of the components were ground in a ball mill until the solid granules were reduced to less than about 10 micrometer. The aqueous suspension could be used directly.

(c) Bait formulation

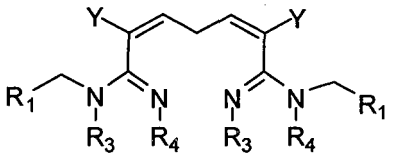
[0107] The following components were prepared: 0.1-10 wt% of any compound selected from compounds 1-73; 80 wt% wheat flour and 19.9-10 wt% molasses. All of the components were sufficiently mixed and shaped according to the need. The edible bait could be oral ingested or distributed to domestic or industrial places such as kitchen, hospital, store and outdoor area infected by public health insects.

Claims

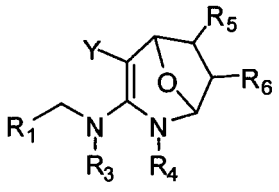
1. A compound of formula (A), (B), (C) or (D), its optical isomer, cis-trans isomer, or its agrochemically acceptable salts thereof,



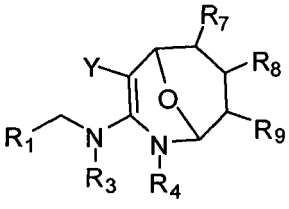
(A)



(B)



(C)



(D)

wherein R_1 is 5 or 6 membered heterocycle containing nitrogen, oxygen and/or sulfur atom, halo-substituted 5 or 6 membered heterocycle containing nitrogen, oxygen and/or sulfur atom, substituted or unsubstituted phenyl, wherein the substituents are one or more groups selected from the group consisting of halogen atoms, C_{1-4} halo-alkyl or C_{1-4} chloro-alkoxyl;

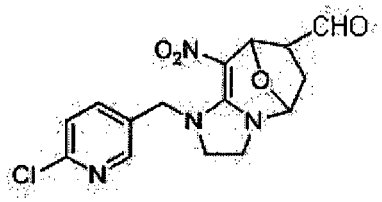
R_2 is H, C_{1-8} saturated or unsaturated alkyl, halo-substituted C_{1-8} saturated or unsaturated alkyl, $-CH_2CH_2OCH_2CH_3$, $-CH_2CH_2OCH_3$, C_{1-4} alkyl-carbonyl, C_{1-4} alkyl-sulfonyl, phenyl, unsubstituted benzyl or benzyl substituted by one or more groups selected from the group consisting of halogen atom, C_{1-4} halo-alkyl or C_{1-4} chloro-alkoxyl;

R_3 and R_4 are independently selected from H, C_{1-6} alkyl, allyl, benzyl, C_{1-4} alkoxyl-C_{1-4} alkyl, C_{1-4} alkoxyl-

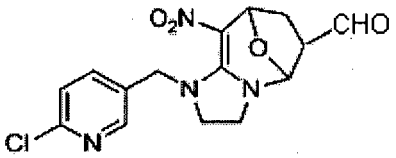
carbonyl, phenoxycarbonyl, C_{2-6} alkynyl-carbonyl, C_{2-3} alkenyl-carbonyl, C_{3-6} cycloalkyl-carbonyl, unsubstitued benzoyl group or benzoyl group substituted by one or more groups selected from the group consisting of halogen atoms, C_{1-4} alkyl, C_{1-4} halo-alkyl, C_{1-4} alkoxyl or C_{1-4} alkyl-carbonyl, furan carbonyl or N, N-dimethylamino carbonyl; or R_3 and R_4 together form $-CH_2-CH_2-$, $-CH_2-CH_2-CH_2-$ or $-CH_2-XR-CH_2-$, wherein X represents heteroatom; R is substituent on X and selected from H, C_{1-6} alkyl, allyl, benzyl, phenyl, C_{1-4} alkoxyl-C_{1-4} alkyl, C_{1-4} alkoxyl-carbonyl, phenoxycarbonyl, C_{2-6} alkynyl-carbonyl, C_{2-3} alkenyl-carbonyl, C_{3-6} cycloalkyl-carbonyl, unsubstitued benzoyl group or benzoyl group substituted by one or more groups selected from the group consisting of halogen atoms, C_{1-4} halo-alkyl, C_{1-8} saturated or unsaturated alkyl or alkoxyl, or C_{1-4} alkyl-carbonyl, furan carbonyl or N, N-dimethylamino carbonyl.

R_5, R_6, R_7, R_8 and R_9 are H, saturated or unsaturated C_{1-4} alkyl, halogen, saturated or unsaturated C_{1-8} alkoxyl, saturated or unsaturated C_{1-4} halo-alkoxyl, C_{1-4} alkyl-carbonyl, C_{1-4} alkyl-sulfonyl, phenyl or benzyl;

Y is nitro, cyano, trifluoromethyl, trifluoroacetyl, or trifluoromethylsulfonyl; or the compound is Compound No. 71 or Compound No. 73;



Compound No. 71



Compound No. 73.

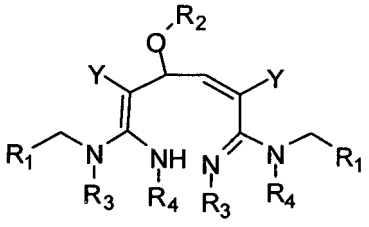
2. The compound, its optical isomer or cis-trans isomer, or its agrochemically acceptable salts of claim 1 wherein R_1 is selected from pyridyl, thiazolyl, pyrimidinyl, tetrahydrofuryl, oxazolyl, or the halogenated groups thereof.

3. The compound, its optical isomer or cis-trans isomer, or its agrochemically acceptable salts of claim 1 wherein R_2 represents H, saturated or unsaturated C_{1-4} alkyl, saturated or unsaturated C_{1-4} halo-alkyl, C_{1-4} alkyl-carbonyl, unsubstituted benzyl or benzyl substituted by one or more groups selected from the group consisting of halogen atom, C_{1-4} halo-alkyl or C_{1-4} chloro-alkoxyl.

4. The compound, its optical isomer or cis-trans isomer, or its agrochemically acceptable salts of claim 1 were featured with that R_3 and R_4 are H, C_{1-6} alkyl group, or R_3 and R_4 together form $-CH_2-CH_2-$ or $-CH_2-CH_2-CH_2-$.

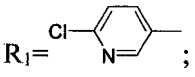
5. The compound, its optical isomer or cis-trans isomer, or its agrochemically acceptable salts of claim 1 wherein R_5, R_6, R_7, R_8 and R_9 are H, saturated or unsaturated C_{1-2} alkyl, halogen, saturated or unsaturated C_{1-4} alkoxyl, saturated or unsaturated C_{1-2} halo-alkoxyl, or C_{1-2} alkyl-sulfonyl.

6. The compound, its optical isomer or cis-trans isomer, or its agrochemically acceptable salts of claim 1 wherein the compound is selected from the group consisting of compounds No. 1-81:



(A)

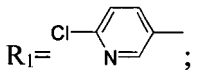
Compound No.1, wherein



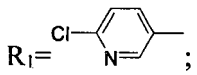
;

R_2=H; R_3=C_2H_5; R_4=CH_3; and Y=NO_2;

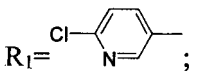
Compound No.2, wherein

R_1=  ;

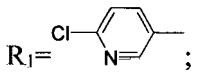
R_2=CH_3; R_3=C_2H_5; R_4=CH_3; and Y=NO_2;
Compound No.3, wherein

R_1=  ;

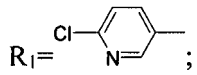
R_2=C_2H_5; R_3=C_2H_5; R_4=CH_3; and Y=NO_2;
Compound No.4, wherein

R_1=  ;

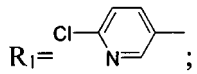
R_2=C_3H_7; R_3=C_2H_5; R_4=CH_3; and Y=NO_2;
Compound No.5, wherein

R_1=  ;

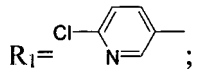
R_2=*i*-C_3H_7; R_3=C_2H_5; R_4=CH_3; and Y=NO_2;
Compound No.6, wherein

R_1=  ;

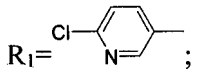
R_2=benzyl; R_3=C_2H_5; R_4=CH_3; and Y=NO_2;
Compound No.7, wherein

R_1=  ;

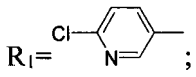
R_2=H; R_3=H; R_4=CH_3; and Y=NO_2;
Compound No.8, wherein

R_1=  ;

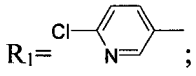
R_2=CH_3; R_3=H; R_4=CH_3; and Y=NO_2;
Compound No.9, wherein

R_1=  ;

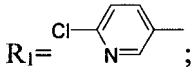
R_2=C_2H_5; R_3=H; R_4=CH_3; and Y=NO_2;
Compound No. 10, wherein



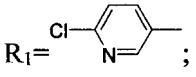
R_2=C_3H_7; R_3=H; R_4=CH_3; and Y=NO_2;
Compound No.11, wherein



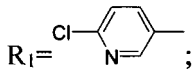
R_2=*i*-C_3H_7; R_3=H; R_4=CH_3; and Y=NO_2;
Compound No. 12, wherein



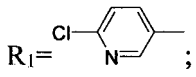
R_2=benzyl; R_3=H; R_4=CH_3; and Y=NO_2;
Compound No. 13, wherein



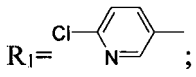
R_2=H; R_3 and R_4 together form -CH_2-CH_2-; and Y=NO_2;
Compound No. 14, wherein



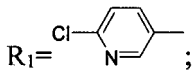
R_2=CH_3; R_3 and R_4 together form -CH_2-CH_2-; and Y=NO_2;
Compound No. 15, wherein



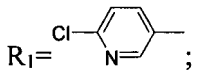
R_2=C_2H_5; R_3 and R_4 together form -CH_2-CH_2-; and Y=NO_2;
Compound No. 16, wherein



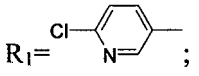
R_2=C_3H_7; R_3 and R_4 together form -CH_2-CH_2-; and Y=NO_2;
Compound No. 17, wherein



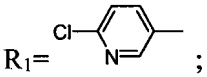
R_2=*i*-C_3H_7; R_3 and R_4 together form -CH_2-CH_2-; and Y=NO_2;
Compound No. 8, wherein



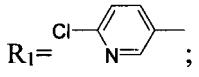
R_2=benzyl; R_3 and R_4 together form -CH_2-CH_2-; and Y=NO_2;
Compound No.19, wherein



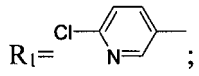
R_2=H; R_3 and R_4 together form -CH_2-CH_2-; and Y=CN;
Compound No.20, wherein



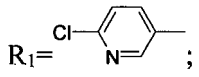
R_2=H; R_3 and R_4 together form -CH_2-CH_2-; and Y=CN;
Compound No.21, wherein



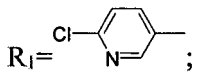
R_2=H; R_3 and R_4 together form -CH_2-CH_2-; and Y=CN;
Compound No.22, wherein



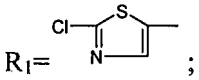
R_2=H; R_3 and R_4 together form -CH_2-CH_2-; and Y=CN;
Compound No.23, wherein



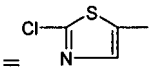
R_2=H; R_3 and R_4 together form -CH_2-CH_2-; and Y=CN;
Compound No.24, wherein



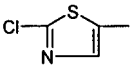
R_2=H; R_3 and R_4 together form -CH_2-CH_2-; and Y=CN;
Compound No.25, wherein



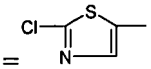
R_2=H; R_3 and R_4 together form -CH_2-CH_2-; and Y=NO_2;
Compound No.26, wherein

R_1=  ;

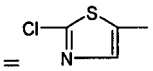
R_2=H; R_3 and R_4 together fonn -CH_2-CH_2-; and Y=NO_2;
Compound No.27, wherein

R_1=  ;

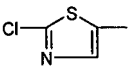
R_2=H; R_3 and R_4 together form -CH_2-CH_2-; and Y=NO_2;
Compound No.28, wherein

R_1=  ;

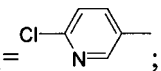
R_2=H; R_3 and R_4 together form -CH_2-CH_2-; and Y=NO_2;
Compound No.29, wherein

R_1=  ;

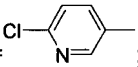
R_2=H; R_3 and R_4 together form -CH_2-CH_2-; and Y=NO_2;
Compound No.30, wherein

R_1=  ;

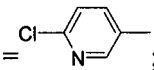
R_2=H; R_3 and R_4 together form -CH_2-CH_2-CH_2-; and Y=NO_2;
Compound No.31, wherein

R_1=  ;

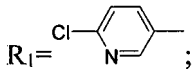
R_2=H; R_3 and R_4 together form -CH_2-CH_2-CH_2-; and Y=NO_2;
Compound No.32, wherein

R_1=  ;

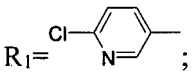
R_2=H; R_3 and R_4 together form -CH_2-CH_2-CH_2-; and Y=NO_2;
Compound No.33, wherein

R_1=  ;

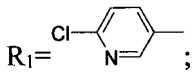
R_2=H; R_3 and R_4 together form -CH_2-CH_2-CH_2-; and Y=NO_2;
Compound No.34, wherein



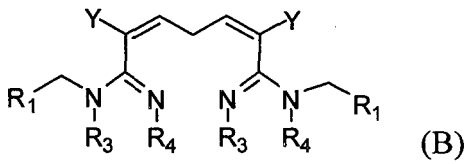
R_2=H; R_3 and R_4 together form -CH_2-CH_2-CH_2-; and Y=NO_2;
Compound No.35, wherein



R_2=H; R_3 and R_4 together form -CH_2-CH_2-CH_2-; and Y=NO_2;
Compound No.36, wherein

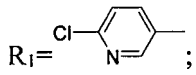


R_2=H; R_3 and R_4 together form -CH_2-CH_2-CH_2-; and Y=NO_2;

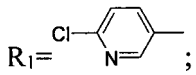


(B)

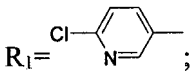
Compound No.37, wherein



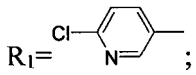
; R_3=C_2H_5; R_4=CH_3; and Y=NO_2;
Compound No.38, wherein



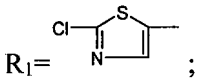
R_3=H; R_4=CH_3; and Y=NO_2;
Compound No.39, wherein



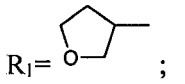
R_3 and R_4 together form -CH_2-CH_2-; and Y=NO_2;
Compound No.40, wherein



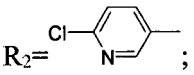
R_3 and R_4 together form -CH_2-CH_2-; and Y=CN;
Compound No.41, wherein



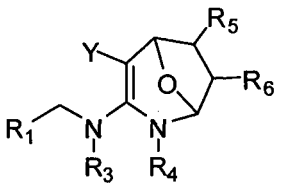
R_3 and R_4 together form $-CH_2-CH_2-$; and $Y=NO_2$;
Compound No.42, wherein



R_3 and R_4 together form $-CH_2-CH_2-$; and $Y=NO_2$;
Compound No.43, wherein

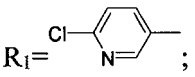


R_3 and R_4 together form $-CH_2-CH_2-CH_2-$; and $Y=NO_2$;

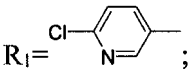


(C)

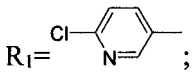
Compound No.44, wherein



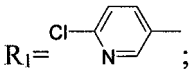
R_3=H; R_4=CH_3; R_5=H; R_6=H; and $Y=NO_2$;
Compound No.45, wherein



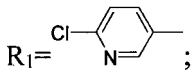
R_3=CH_3; R_4=CH_3; R_5=H; R_6=H; and $Y=NO_2$;
Compound No.46, wherein



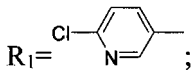
R_3=C_2H_5; R_4=CH_3; R_5=H; R_6=H; and $Y=NO_2$;
Compound No.47, wherein



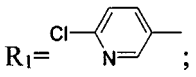
R_3=H; R_4=H; R_5=H; R_6=H; and $Y=NO_2$;
Compound No.48, wherein



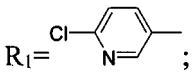
R_3=CH_3; R_4=H; R_5=H; R_6=H; and Y=NO_2;
Compound No.49, wherein



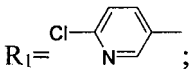
R_3=C_2H_5; R_4=H; R_5=H; R_6=H; and Y=NO_2;
Compound No.50, wherein



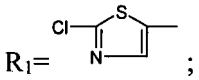
R_3=CH_3; R_4=C_2H_5; R_5=H; R_6=H; and Y=NO_2;
Compound No.51, wherein



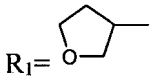
R_3=C_2H_5; R_4=C_2H_5; R_5=H; R_6=H; and Y=NO_2;
Compound No.52, wherein



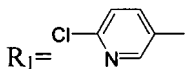
R_3 and R_4 together form -CH_2-CH_2-; R_5=H; R_6=H; and Y=NO_2;
Compound No.53, wherein



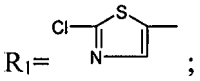
R_3 and R_4 together form -CH_2-CH_2-; R_5=H; R_6=H; and Y=NO_2;
Compound No.54, wherein



R_3 and R_4 together form -CH_2-CH_2-; R_5=H; R_6=H; and Y=NO_2;
Compound No.55, wherein Y=NO_2;

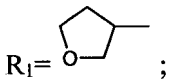


R_3 and R_4 together form -CH_2-CH_2-; R_5=CH_3; R_6=CH_3; and
Compound No.56, wherein Y=NO_2;



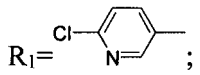
;

R_3 and R_4 together form $-CH_2-CH_2-$; $R_5=CH_3$; $R_6=CH_3$; and Compound No.57, wherein $Y=NO_2$;



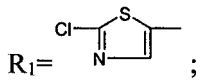
;

R_3 and R_4 together form $-CH_2-CH_2-$; $R_5=CH_3$; $R_6=CH_3$; and Compound No.58, wherein



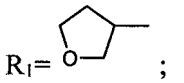
;

R_3 and R_4 together form $-CH_2-CH_2-$; $R_5=F$; $R_6=F$; and $Y=NO_2$; Compound No.59, wherein



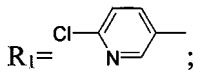
;

R_3 and R_4 together form $-CH_2-CH_2-$; $R_5=F$; $R_6=F$; and $Y=NO_2$; Compound No.60, wherein



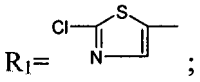
;

R_3 and R_4 together form $-CH_2-CH_2-$; $R_5=F$; $R_6=F$; and $Y=NO_2$; Compound No.61, wherein $Y=NO_2$;



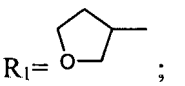
;

R_3 and R_4 together form $-CH_2-CH_2-CH_2-$; $R_5=H$; $R_6=H$; and Compound No.62, wherein $Y=NO_2$;



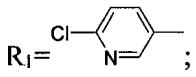
;

R_3 and R_4 together form $-CH_2-CH_2-CH_2-$; $R_5=H$; $R_6=H$; and Compound No.63, wherein $Y=NO_2$;

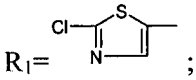


;

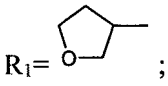
R_3 and R_4 together form $-CH_2-CH_2-CH_2-$; $R_5=H$; $R_6=H$; and Compound No.64, wherein



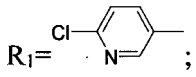
R_3 and R_4 together form $-CH_2-CH_2-$; R_5=H; R_6=H; and Y=CN; Compound No.65, wherein



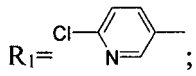
R_3 and R_4 together form $-CH_2-CH_2-$; R_5=H; R_6=H; and Y=CN; Compound No.66, wherein



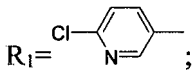
R_3 and R_4 together form $-CH_2-CH_2-$; R_5=H; R_6=H; and Y=CN; Compound No.67, wherein Y=NO_2;



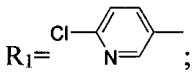
R_3 and R_4 together form $-CH_2-CH_2-$; R_5=H; R_6=CH_3O; and Compound No.68, wherein Y=NO_2;



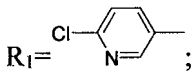
R_3 and R_4 together form $-CH_2-CH_2-$; R_5=H; R_6=C_2H_5O; and Compound No.69, wherein Y=NO_2;



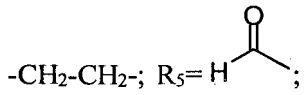
R_3 and R_4 together form $-CH_2-CH_2-$; R_5=CH_3O; R_6=H; and Compound No.70, wherein Y=NO_2;



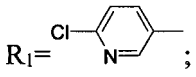
R_3 and R_4 together form $-CH_2-CH_2-$; R_5=C_2H_5O; R_6=H; and Compound No.71, wherein Y=NO_2;



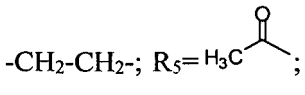
R_3 and R_4 together form



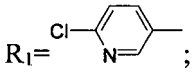
R_6=H; and
Compound No.72, wherein Y=NO_2;



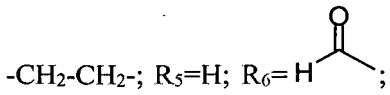
R_3 and R_4 together form



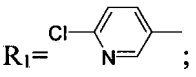
R_6=H; and
Compound No.73, wherein Y=NO_2;



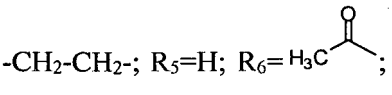
R_3 and R_4 together form



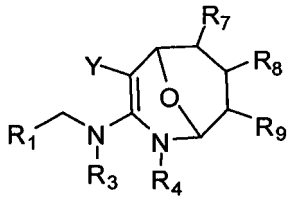
and
Compound No.74, wherein Y=NO_2;



R_3 and R_4 together form

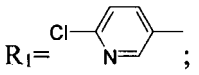


and

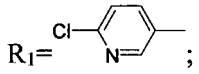


(D)

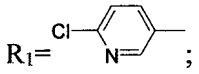
Compound No.75, wherein



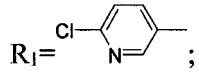
$R_3=C_2H_5$; $R_4=CH_3$; $R_7=R_8=R_9=H$; and $Y=NO_2$;
Compound No.76, wherein



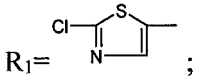
$R_3=H$; $R_4=CH_3$; $R_7=R_8=R_9=H$; and $Y=NO_2$;
Compound No.77, wherein



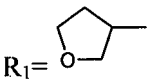
R_3 and R_4 together form $-CH_2-CH_2-$; $R_7=R_8=R_9=H$; and $Y=NO_2$;
Compound No.78, wherein



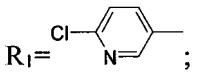
R_3 and R_4 together form $-CH_2-CH_2-$; $R_7=R_8=R_9=H$; and $Y=CN$;
Compound No.79, wherein



R_3 and R_4 together form $-CH_2-CH_2-$; $R_7=R_8=R_{-9}=H$; and $Y=NO_2$;
Compound No.80, wherein



R_3 and R_4 together form $-CH_2-CH_2-$; $R_7=R_8=R_9=H$; and $Y=NO_2$;
Compound No.81, wherein



R_3 and R_4 together form $-CH_2-CH_2-CH_2-$; $R_7=R_8=R_9=H$; and $Y=NO_2$.

7. The compound, its optical isomer or cis-trans isomer, or its agrochemically acceptable salts of claim 1 wherein Y is nitro group or cyano group.

8. An agrochemical composition comprising:

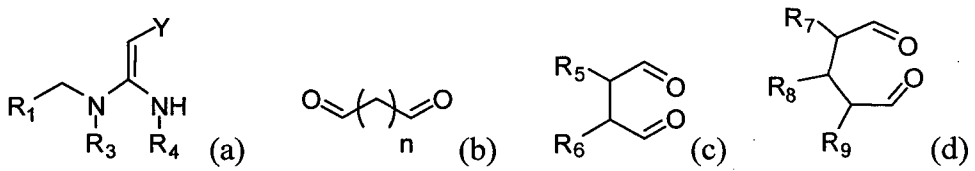
(a) 0.001-99.99wt% of the compound, its optical isomer, cis-trans isomer, agrochemically acceptable salts thereof according to any of claims 1-7 or the combination thereof; and
(b) an agrochemically acceptable carrier or excipient.

9. An use of the agrochemical composition of claim 8 in killing or controlling agricultural pests, animal health hazard

pests and sanitary pests; or use of the agrochemical composition of claim 8 as an insecticidal composition for killing or controlling agricultural pests, sanitary pests and animal health hazard pests.

10. A method for preparation of the compound, its optical isomer or cis-trans isomer, or an agrochemically acceptable salts according to any of claims 1-7, wherein the method comprises the following steps:

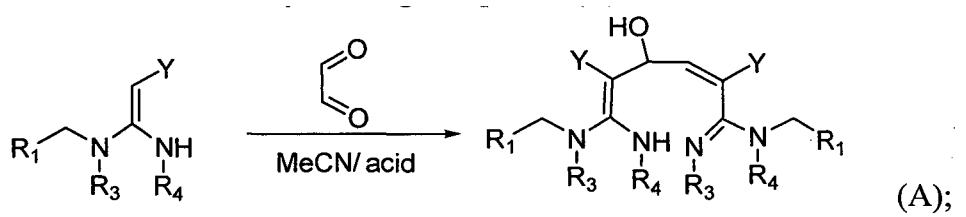
in the presence of catalytic acid and at 0-60 °C, reacting compound of formula (a) with compound (b), (c) or (d), thereby forming compound (A), (B), (C) or (D), wherein R_2 represents H,



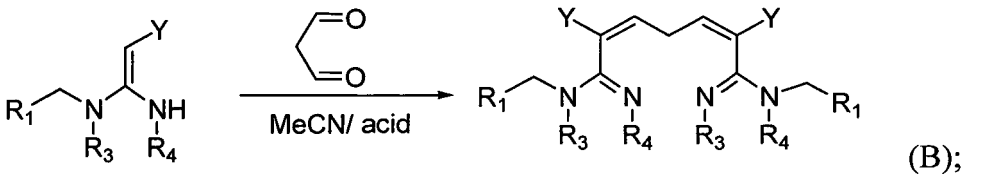
wherein R_1, R_3, R_4, R_5, R_6, R_7, R_8, R_9 and Y are defined as in claim 1, and n is 0 or 1.

11. The method of claim 10 wherein the method comprises:

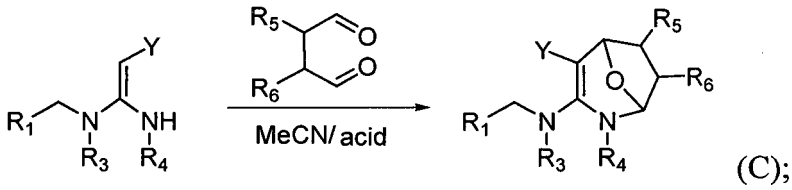
in the presence of catalytic acid, the following reaction is carried out at 20-30 °C in acetonitrile for 2-24 hours, thereby forming compound (A), wherein R_2 is H:



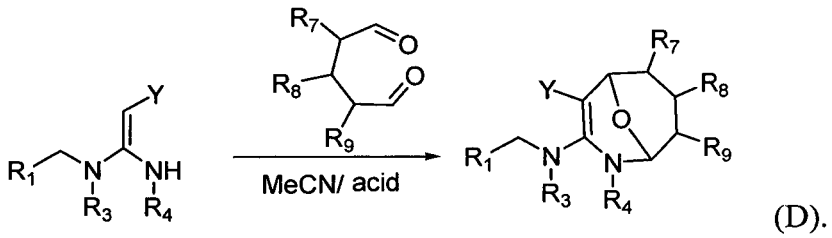
in the presence of catalytic acid, the following reaction is carried out at 20-30 °C in acetonitrile for 2-24 hours, thereby forming compound (B):



in the presence of catalytic acid, the following reaction is carried out at 10-50 °C in acetonitrile for 2-24 hours, thereby forming compound (C):



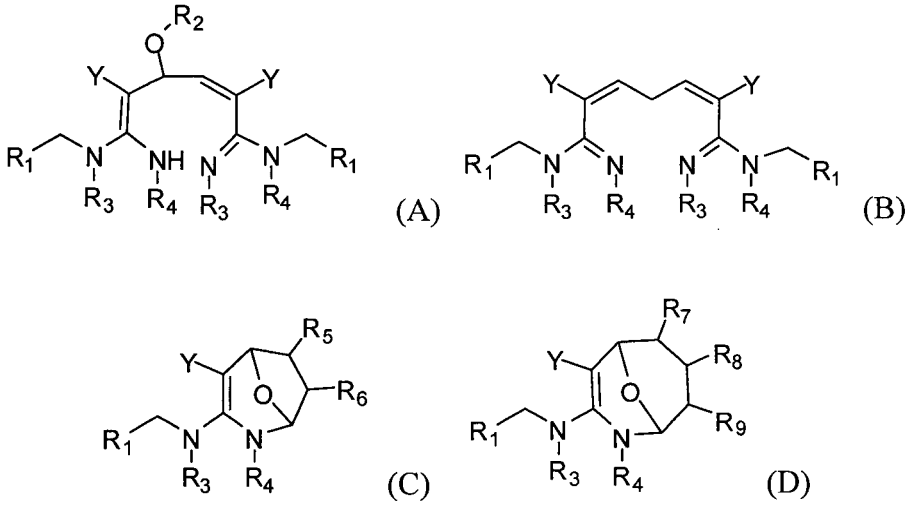
in the presence of catalytic acid, the following reaction is carried out at 10-50 °C in acetonitrile for 2-24 hours, thereby forming compound (D):



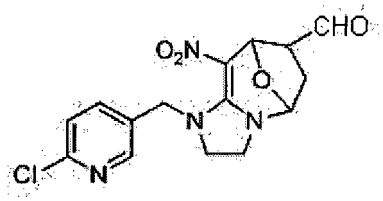
(D).

Patentansprüche

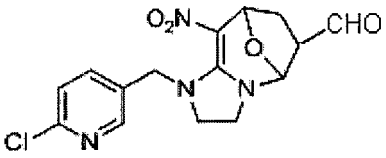
1. Verbindung der Formel (A), (B), (C) oder (D), dessen optisches Isomer, cis-trans-Isomer, oder agrochemisch annehmbare Salze davon,



wobei R_1 ein 5 oder 6 gliedriger Heterozyklus enthaltend Stickstoff, Sauerstoff und/oder Schwefelatom, ein halosubstuierter 5 oder 6 gliedriger Heterozyklus enthaltend Stickstoff, Sauerstoff und/oder Schwefelatom, substituertes oder unsubstituiertes Phenyl, wobei die Substituenten ein oder mehrere Gruppen ausgewählt aus der Gruppe bestehend aus Halogenatomen, C_{1-4} Halo-alkyl oder C_{1-4} Chloro-alkoxyl sind, ist;
R_2 ist H, C_{1-8} gesättigtes oder ungesättigtes Alkyl, Halo-substituiertes C_{1-8} gesättigtes oder ungesättigtes Alkyl, $-CH_2CH_2OCH_2CH_3$, $-CH_2CH_2OCH_3$, C_{1-4} Alkyl-carbonyl, C_{1-4} Alkyl-sulfonyl, Phenyl, unsubstituiertes Benzyl oder Benzyl substituiert mit ein oder mehreren Gruppen ausgewählt aus Gruppen bestehend aus Halogenatome, C_{1-4} Halo-alkyl oder C_{1-4} Chlor-alkoxyl;
R_3 und R_4 sind unabhängig voneinander ausgewählt aus H, C_{1-6} Alkyl, Allyl, Benzyl, C_{1-4} Alkoxyl-C_{1-4} Alkyl, C_{1-4} Alkoxyl-carbonyl, Phenoxycarbonyl, C_{2-6} Alkinyl-carbonyl, C_{2-3} Alkenyl-carbonyl, C_{3-6} Cycloalkyl-carbonyl, unsubstituierte Benzoylgruppe oder Benzoylgruppe substituiert mit ein oder mehreren Gruppen ausgewählt aus der Gruppe bestehend aus Halogenatom, C_{1-4} Alkyl, C_{1-4} Halo-alkyl, C_{1-4} Alkoxyl oder C_{1-4} Alkyl-carbonyl, Furancarbonyl oder N,N-dimehtylamino carbonyl; oder R_3 und R_4 bilden zusammen $-CH_2-CH_2-$, $-CH_2-CH_2-CH_2-$ oder $-CH_2-XR-CH_2-$, wobei X ein Heteroatom darstellt; R ist ein Substituent von X und ausgewählt aus H, C_{1-6} Alkyl, Allyl, Benzyl, Phenyl, C_{1-4} Alkoxyl-C_{1-4} Alkyl, C_{1-4} Alkoxyl-carbonyl, Phenoxycarbonyl, C_{2-6} Alkinyl-carbonyl, C_{2-3} Alkenyl-carbonyl, C_{3-6} Cycloalkyl-carbonyl, unsubstituerter Benzoyl Gruppe oder Benzoyl Gruppe substituiert mit ein oder mehreren Gruppen ausgewählt aus der Gruppe bestehend aus Halogenatomen, C_{1-4} Halo-alkyl, C_{1-8} gesättigten oder ungesättigten Alkyl oder Alkoxyl, oder C_{1-4} Alkyl-carbonyl, Furan carbonyl oder N,N-dimethylamino carbonyl,
R_5, R_6, R_7, R_8 und R_9 sind H, gesättigt oder ungesättigtes C_{1-4} Alkyl, Halogen, gesättigt oder ungesättigtes C_{1-8} Alkoxyl, gesättigtes oder ungesättigtes C_{1-4} Halo-alkoxyl, C_{1-4} Alkyl-carbonyl, C_{1-4} Alkyl-sulfonyl, Phenyl oder Benzyl;
Y ist Nitro, Cyano, Trifluoromethyl, Trifluoroacetyl, oder Trifluoromethylsulfonyl; oder die Verbindung ist die Verbindung Nr. 71 oder Nr. 73:



Verbindung Nr. 71



Verbindung Nr. 73.

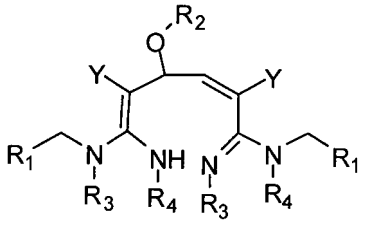
2. Die Verbindung, dessen optisches Isomer oder cis-trans-Isomer, oder agrochemisch annehmbare Salze gemäß Anspruch 1, wobei R_1 ausgewählt ist aus Pyridyl, Thiazolyl, Pyrimidinyl, Tetrahydrofuryl, Oxazolyl, oder die halogenierten Gruppen davon.

3. Die Verbindung, dessen optisches Isomer oder cis-trans-Isomer, oder agrochemisch annehmbare Salze gemäß Anspruch 1, wobei R_2 H, gesättigtes oder ungesättigtes C_{1-4} Alkyl, gesättigtes oder ungesättigtes C_{1-4} Halo-alkyl, C_{1-4} Alkyl-carbonyl, unsubstituiertes Benzyl oder Benzyl mit ein oder mehreren Gruppen ausgewählt aus der Gruppe bestehend aus Halogenatome, C_{1-4} Halo-alkyl oder C_{1-4} Chlor-alkoxyl darstellt.

4. Die Verbindung, dessen optisches Isomer oder cis-trans-Isomer, oder agrochemisch annehmbare Salze gemäß Anspruch 1, wobei R_3 und R_4 H, C_{1-6} Alkyl Gruppe sind oder R_3 und R_4 bilden zusammen $-CH_2-CH_2-$ oder $-CH_2-CH_2-CH_2-$.

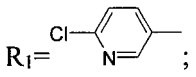
5. Die Verbindung, dessen optisches Isomer oder cis-trans-Isomer, oder agrochemisch annehmbare Salze gemäß Anspruch 1, wobei R_5, R_6, R_7, R_8 und R_9 H, gesättigtes oder ungesättigtes C_{1-2} Alkyl, Halogen, gesättigtes oder ungesättigtes C_{1-4} Alkoxyl, gesättigtes oder ungesättigtes C_{1-2} Halo-alkoxyl, oder C_{1-2} Alkyl-sulfonyl ist.

6. Die Verbindung, dessen optisches Isomer oder cis-trans-Isomer, oder agrochemisch annehmbare Salze gemäß Anspruch 1, wobei die Verbindung ausgewählt ist aus der Gruppe bestehend aus Verbindungen Nr. 1-81:



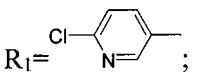
(A)

Verbindung Nr. 1, wobei



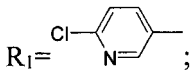
;

R_2=H; R_3=C_2H_5; R_4=CH_3; und Y=NO_2;
Verbindung Nr. 2, wobei

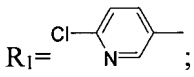


;

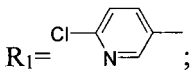
R_2=CH_3; R_3=C_2H_5; R_4=CH_3; und Y=NO_2;
Verbindung Nr. 3, wobei

R_1=  ;

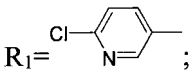
R_2=C_2H_5; R_3=C_2H_5; R_4=CH_3; und Y=NO_2;
Verbindung Nr. 4, wobei

R_1=  ;

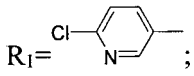
R_2=C_3H_7; R_3=C_2H_5; R_4=CH_3; und Y=NO_2;
Verbindung Nr. 5, wobei

R_1=  ;

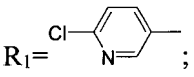
R_2=i-C_3H_7; R_3=C_2H_5; R_4=CH_3; und Y=NO_2;
Verbindung Nr. 6, wobei

R_1=  ;

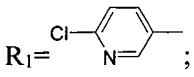
R_2=Benzyl; R_3=C_2H_5; R_4=CH_3; und Y=NO_2;
Verbindung Nr. 7, wobei

R_1=  ;

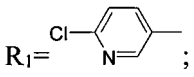
R_2=H; R_3=H; R_4=CH_3; und Y=NO_2;
Verbindung Nr. 8, wobei

R_1=  ;

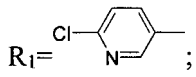
R_2=CH_3; R_3=H; R_4=CH_3; und Y=NO_2;
Verbindung Nr. 9, wobei

R_1=  ;

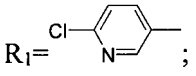
R_2=C_2H_5; R_3=H; R_4=CH_3; und Y=NO_2;
Verbindung Nr. 10, wobei

R_1=  ;

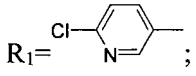
R_2=C_3H_7; R_3=H; R_4=CH_3; und Y=NO_2;
Verbindung Nr. 11, wobei



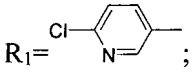
R_2=i-C_3H_7; R_3=H; R_4=CH_3; und Y=NO_2;
Verbindung Nr. 12, wobei



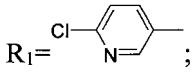
R_2=Benzyl; R_3=H; R_4=CH_3; und Y=NO_2;
Verbindung Nr. 13, wobei



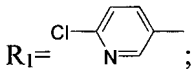
R_2=H; R_3 und R_4 bilden zusammen -CH_2-CH_2-; und Y=NO_2;
Verbindung Nr. 14, wobei



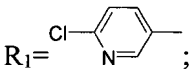
R_2=CH_3; R_3 und R_4 bilden zusammen -CH_2-CH_2-; und Y=NO_2;
Verbindung Nr. 15, wobei



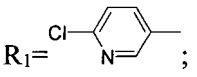
R_2=C_2H_5; R_3 und R_4 bilden zusammen -CH_2-CH_2-; und Y=NO_2;
Verbindung Nr. 16, wobei



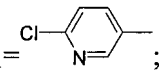
R_2=C_3H_7; R_3 und R_4 bilden zusammen -CH_2-CH_2-; und Y=NO_2;
Verbindung Nr.17, wobei



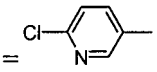
R_2=*i*-C_3H_7; R_3 und R_4 bilden zusammen -CH_2-CH_2-; und Y=NO_2;
Verbindung Nr.18, wobei



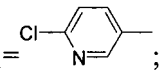
R_2=Benzyl; R_3 und R_4 bilden zusammen -CH_2-CH_2-; und Y=NO_2;
Verbindung Nr.19, wobei

R_1=  ;

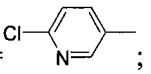
R_2=H; R_3 und R_4 bilden zusammen -CH_2-CH_2-; und Y=CN;
Verbindung Nr.20, wobei

R_1=  ;

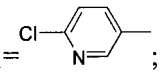
R_2=H; R_3 und R_4 bilden zusammen -CH_2-CH_2-; und Y=CN;
Verbindung Nr.21, wobei

R_1=  ;

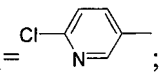
R_2=H; R_3 und R_4 bilden zusammen -CH_2-CH_2-; und Y=CN;
Verbindung Nr.22, wobei

R_1=  ;

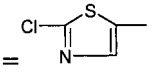
R_2=H; R_3 und R_4 bilden zusammen -CH_2-CH_2-; und Y=CN;
Verbindung Nr.23, wobei

R_1=  ;

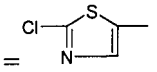
R_2=H; R_3 und R_4 bilden zusammen -CH_2-CH_2-; und Y=CN;
Verbindung Nr.24, wobei

R_1=  ;

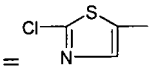
R_2=H; R_3 und R_4 bilden zusammen -CH_2-CH_2-; und Y=CN;
Verbindung Nr.25, wobei

R_1=  ;

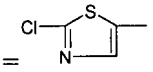
R_2=H; R_3 und R_4 bilden zusammen -CH_2-CH_2-; und Y=NO_2;
Verbindung Nr.26, wobei

R_1=  ;

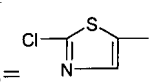
R_2=H; R_3 und R_4 bilden zusammen -CH_2-CH_2-; und Y=NO_2;
Verbindung Nr.27, wobei

R_1=  ;

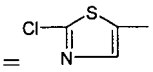
R_2=H; R_3 und R_4 bilden zusammen -CH_2-CH_2-; und Y=NO_2;
Verbindung Nr.28, wobei

R_1=  ;

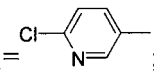
R_2=H; R_3 und R_4 bilden zusammen -CH_2-CH_2-; und Y=NO_2;
Verbindung Nr.29, wobei

R_1=  ;

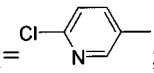
R_2=H; R_3 und R_4 bilden zusammen -CH_2-CH_2-; und Y=NO_2;
Verbindung Nr.30, wobei

R_1=  ;

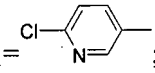
R_2=H; R_3 und R_4 bilden zusammen -CH_2-CH_2-CH_2-; und Y=NO_2;
Verbindung Nr.31, wobei

R_1=  ;

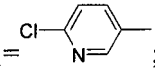
R_2=H; R_3 und R_4 bilden zusammen -CH_2-CH_2-CH_2-; und Y=NO_2;
Verbindung Nr.32, wobei

R_1=  ;

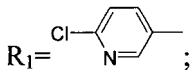
R_2=H; R_3 und R_4 bilden zusammen -CH_2-CH_2-CH_2-; und Y=NO_2;
Verbindung Nr.33, wobei

R_1=  ;

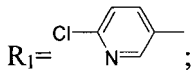
R_2=H; R_3 und R_4 bilden zusammen -CH_2-CH_2-CH_2-; und Y=NO_2;
Verbindung Nr.34, wobei

R_1=  ;

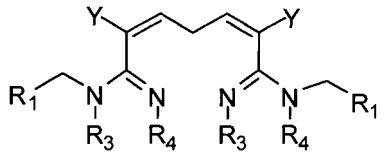
R_2=H; R_3 und R_4 bilden zusammen -CH_2-CH_2-CH_2-; und Y=NO_2;
Verbindung Nr.35, wobei



R_2=H; R_3 und R_4 bilden zusammen -CH_2-CH_2-CH_2-; und Y=NO_2;
Verbindung Nr.36, wobei

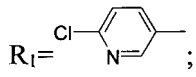


R_2=H; R_3 und R_4 bilden zusammen -CH_2-CH_2-CH_2-; und Y=NO_2;

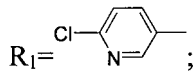


(B)

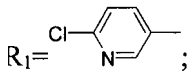
Verbindung Nr.37, wobei



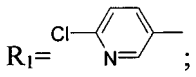
R_3=C_2H_5; R_4=CH_3; und Y=NO_2;
Verbindung Nr.38, wobei



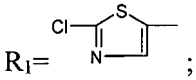
R_3=H; R_4=CH_3; und Y=NO_2;
Verbindung Nr.39, wobei R_1



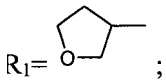
R_3 und R_4 bilden zusammen -CH_2-CH_2-; und Y=NO_2;
Verbindung Nr.40, wobei



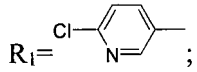
R_3 und R_4 bilden zusammen -CH_2-CH_2-; und Y=CN;
Verbindung Nr.41, wobei



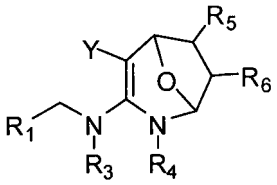
R_3 und R_4 bilden zusammen -CH_2-CH_2-; und Y=NO_2;
Verbindung Nr.42, wobei



R_3 und R_4 bilden zusammen $-CH_2-CH_2-$; und $Y=NO_2$;
Verbindung Nr.43, wobei

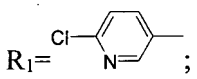


R_3 und R_4 bilden zusammen $-CH_2-CH_2-CH_2-$; und $Y=NO_2$;

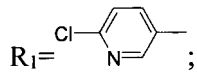


(C)

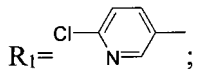
Verbindung Nr.44, wobei



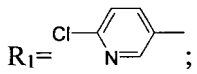
R_3=H; R_4=CH_3; R_5=H; R_6=H; und $Y=NO_2$;
Verbindung Nr.45, wobei



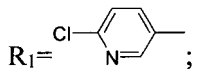
R_3=CH_3; R_4=CH_3; R_5=H; R_6=H; und $Y=NO_2$;
Verbindung Nr.46, wobei



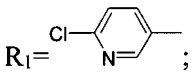
R_3=C_2H_5; R_4=CH_3; R_5=H; R_6=H; und $Y=NO_2$;
Verbindung Nr.47, wobei



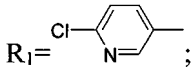
R_3=H; R_4=H; R_5=H; R_6=H; und $Y=NO_2$;
Verbindung Nr.48, wobei



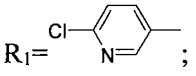
R_3=CH_3; R_4=H; R_5=H; R_6=H; und $Y=NO_2$;
Verbindung Nr.49, wobei



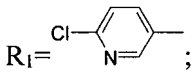
$R_3=C_2H_5$; R_4=H; R_5=H; R_6=H; und Y=NO_2;
Verbindung Nr.50, wobei



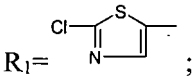
$R_3=CH_3$; $R_4=C_2H_5$; R_5=H; R_6=H; und Y=NO_2;
Verbindung Nr.51, wobei



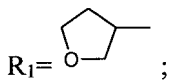
$R_3=C_2H_5$; $R_4=C_2H_5$; R_5=H; R_6=H; und Y=NO_2;
Verbindung Nr.52, wobei Y=NO_2;



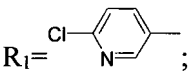
R_3 und R_4 bilden zusammen -CH_2-CH_2-; R_5=H; R_6=H; und
Verbindung Nr.53, wobei Y=NO_2;



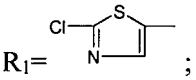
R_3 und R_4 bilden zusammen -CH_2-CH_2-; R_5=H; R_6=H; und
Verbindung Nr.54, wobei



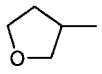
R_3 und R_4 bilden zusammen -CH_2-CH_2-; R_5=H; R_6=H; und Y=NO_2;
Verbindung Nr.55, wobei Y=NO_2;



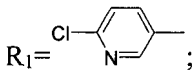
R_3 und R_4 bilden zusammen -CH_2-CH_2-; $R_5=CH_3$; $R_6=CH_3$; und
Verbindung Nr.56, wobei Y=NO_2;



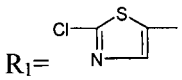
R_3 und R_4 bilden zusammen -CH_2-CH_2-; $R_5=CH_3$; $R_6=CH_3$; und
Verbindung Nr.57, wobei Y=NO_2;

R_1=  ;

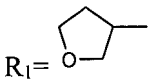
R_3 und R_4 bilden zusammen -CH_2-CH_2-; R_5=CH_3; R_6=CH_3; und Verbindung Nr.58, wobei Y=NO_2;

R_1=  ;

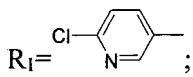
R_3 und R_4 bilden zusammen -CH_2-CH_2-; R_5=F, R_6=F; und Verbindung Nr.59, wobei Y=NO_2;

R_1=  ;

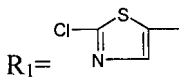
R_3 und R_4 bilden zusammen -CH_2-CH_2-; R_5=F; R_6=F; und Verbindung Nr.60, wobei

R_1=  ;

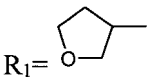
R_3 und R_4 bilden zusammen -CH_2-CH_2-; R_5=F; R_6=F; und Y=NO_2; Verbindung Nr.61, wobei Y=NO_2;

R_1=  ;

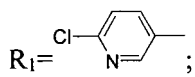
R_3 und R_4 bilden zusammen -CH_2-CH_2-CH_2-; R_5=H; R_6=H; und Verbindung Nr.62, wobei Y=NO_2;

R_1=  ;

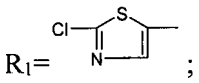
R_3 und R_4 bilden zusammen -CH_2-CH_2-CH_2-; R_5=H; R_6=H; und Verbindung Nr.63, wobei Y=NO_2;

R_1=  ;

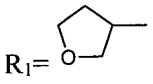
R_3 und R_4 bilden zusammen -CH_2-CH_2-CH_2-; R_5=H; R_6=H; und Verbindung Nr.64, wobei

R_1=  ;

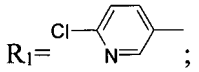
R_3 und R_4 bilden zusammen -CH_2-CH_2-; R_5=H; R_6=H; und Y=CN; Verbindung Nr.65, wobei Y=CN;



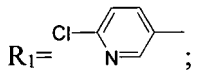
R_3 und R_4 bilden zusammen $-CH_2-CH_2-$; R_5=H; R_6=H; und
Verbindung Nr.66, wobei



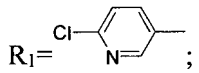
R_3 und R_4 bilden zusammen $-CH_2-CH_2-$; R_5=H; R_6=H; und Y=CN;
Verbindung Nr.67, wobei Y=NO_2;



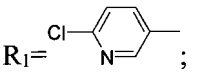
R_3 und R_4 bilden zusammen $-CH_2-CH_2-$; R_5=H; R_6=CH_3O; und
Verbindung Nr.68, wobei Y=NO_2;



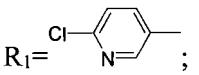
R_3 und R_4 bilden zusammen $-CH_2-CH_2-$; R_5=H; R_6=C_2H_5O; und
Verbindung Nr.69, wobei Y=NO_2;



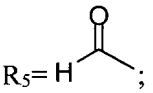
R_3 und R_4 bilden zusammen $-CH_2-CH_2-$; R_5=CH_3O; R_6=H; und
Verbindung Nr.70, wobei Y=NO_2;



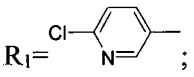
R_3 und R_4 bilden zusammen $-CH_2-CH_2-$; R_5=C_2H_5O; R_6=H; und
Verbindung Nr.71, wobei Y=NO_2;



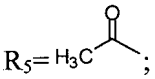
R_3 und R_4 bilden zusammen $-CH_2-CH_2-$;



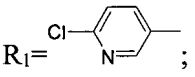
R_6=H; und
Verbindung Nr.72, wobei Y=NO_2;



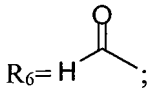
R_3 und R_4 bilden zusammen $-CH_2-CH_2-$;



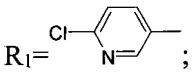
R_6=H; und
Verbindung Nr.73, wobei Y=NO_2;



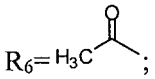
R_3 und R_4 bilden zusammen $-CH_2-CH_2-$; R_5=H;



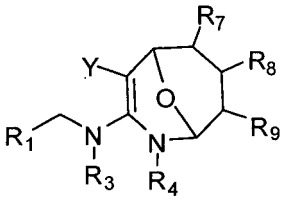
und
Verbindung Nr.74, wobei Y=NO_2;



R_3 und R_4 bilden zusammen $-CH_2-CH_2-$; R_5=H;

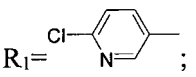


und

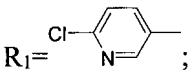


(D)

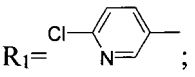
Verbindung Nr.75, wobei



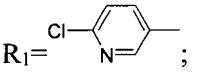
R_3=C_2H_5; R_4=CH_3; R_7=R_8=R_9=H; und Y=NO_2;
Verbindung Nr.76, wobei



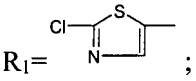
R_3=H; R_4=CH_3; R_7=R_8=R_9=H; und Y=NO_2;
Verbindung Nr.77, wobei Y=NO_2;



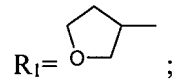
R_3 und R_4 bilden zusammen -CH_2-CH_2-; R_7=R_8=R_9=H; und
Verbindung Nr.78, wobei Y=CN;



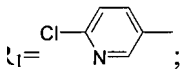
R_3 und R_4 bilden zusammen -CH_2-CH_2-; R_7=R_8=R_9=H; und
Verbindung Nr.79, wobei Y=NO_2;



R_3 und R_4 bilden zusammen -CH_2-CH_2-; R_7=R_8=R_9=H; und
Verbindung Nr.80, wobei



R_3 und R_4 bilden zusammen -CH_2-CH_2-; R_7=R_8=R_9=H; und Y=NO_2;
Verbindung Nr.81, wobei



R_3 und R_4 bilden zusammen -CH_2-CH_2-CH_2-; R_7=R_8=R_9=H; und Y=NO_2.

7. Die Verbindung, dessen optisches Isomer oder cis-trans-Isomer, oder agrochemisch annehmbare Salze gemäß Anspruch 1, wobei Y eine Nitrogruppe oder Cyanogruppe ist.

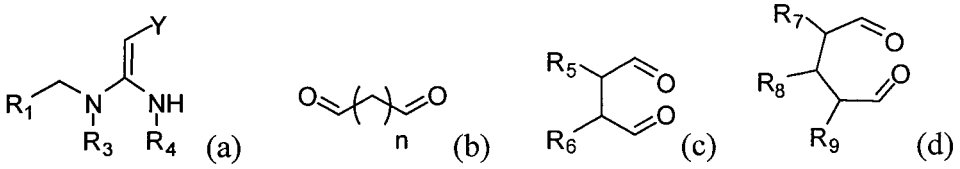
8. Agrochemische Zusammensetzung umfassend:

(a) 0.001-99.99 Gew.-% der Verbindung, dessen optisches Isomer, cis-trans-Isomer, oder agrochemisch annehmbare Salze davon gemäß einem der Ansprüche 1-7 oder eine Kombination davon; und
(b) einen agrochemisch annehmbaren Träger oder Exipienten.

9. Verwendung der agrochemischen Zusammensetzung gemäß Anspruch 8 zum Töten oder zur Kontrolle von Agrarschädlingen, Schädlingen, die die Gesundheit von Tieren gefährden, und Hygieneschädlingen; oder Verwendung der agrochemischen Zusammensetzung gemäß Anspruch 8 als insektizide Zusammensetzung zum Töten oder Kontrollieren von Agrarschädlingen, Hygieneschädlingen und Schädlingen, die die Gesundheit von Tieren gefährden.

10. Verfahren zur Herstellung der Verbindung, dessen optischen Isomer oder cis-trans-Isomer, oder agrochemisch annehmbaren Salzen davon gemäß einem der Ansprüche 1,1-7, wobei das Verfahren die folgenden Schritte umfasst:

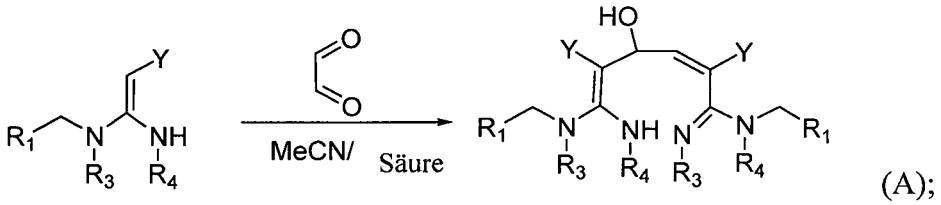
in Anwesenheit einer katalytischen Säure und bei 0-60°C umsetzen der Verbindung gemäß Formel (a) mit der Verbindung (b), (c) oder (d), zur Ausbildung der Verbindung (A), (B), (C) oder (D), wobei R_2 H darstellt,



wobei R_1, R_3, R_4, R_5, R_6, R_7, R_8, R_9 und Y in Anspruch 1 definiert sind und n ist 0 oder 1.

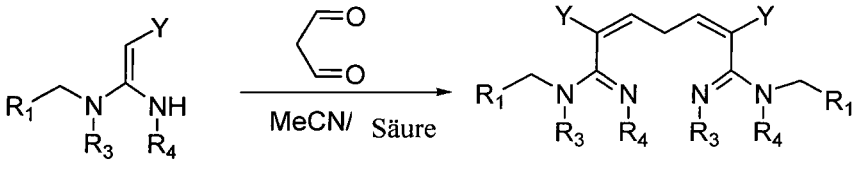
11. Verfahren nach Anspruch 10, wobei das Verfahren ein Ausführen der folgenden Reaktion umfasst:

in Anwesenheit einer katalytischen Säure bei 20-30°C in Acetonitril für 2-24 Stunden, unter Ausbildung der Verbindung (A), wobei R_2 H ist:



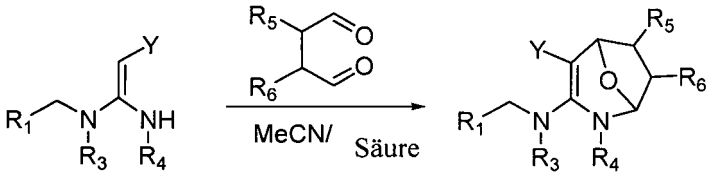
(A);

in Anwesenheit einer katalytischen Säure wird die folgende Reaktion bei 20-30°C in Acetonitrile für 2-24 Stunden, um die Verbindung (B) auszubilden:



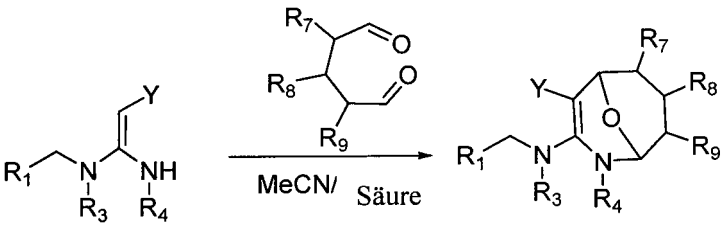
(B);

in Anwesenheit einer katalytischen Säure wird die folgende Reaktion bei 10-50°C in Acetonitrile für 2-24 Stunden ausgeführt, um die Verbindung (C) auszubilden:



(C);

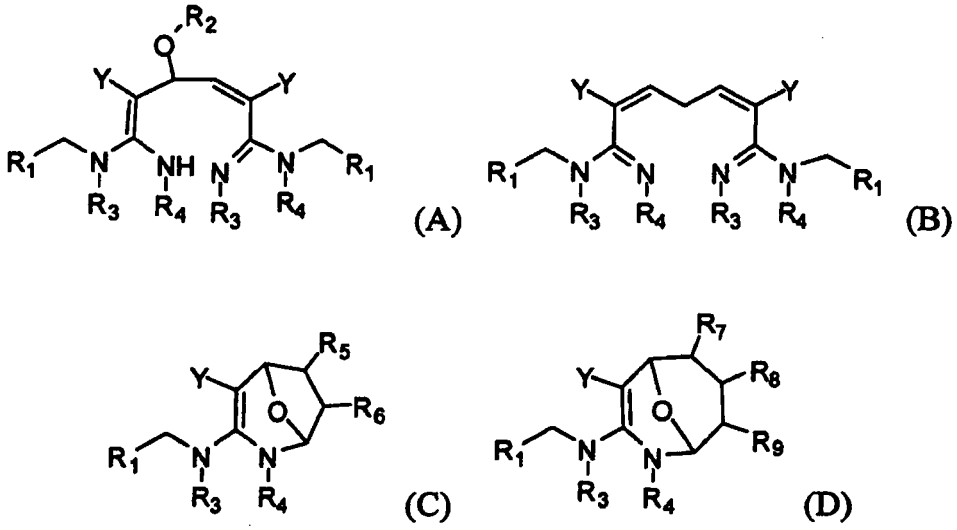
in Anwesenheit einer katalytischen Säure wird die folgende Reaktion bei 10-50°C in Acetonitrile für 2-24 Stunden ausgeführt, um die Verbindung (D) auszubilden:



(D).

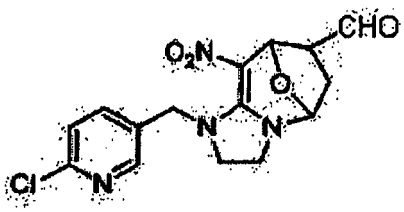
Revendications

1. Composé de formule (A), (B), (C) ou (D), son isomère optique, son isomère cis,trans, ou ses sels acceptables sur le plan agrochimique,

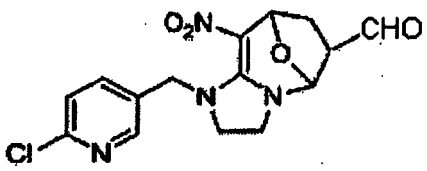


dans lequel

R_1 est un hétérocycle de 5 ou 6 chaînons contenant un atome d'azote, d'oxygène et/ou de soufre, un hétérocycle de 5 ou 6 chaînons substitué par halogéno contenant un atome d'azote, d'oxygène et/ou de soufre, phényle substitué ou non substitué, où les substituants sont un ou plusieurs groupements choisis dans le groupe constitué par des atomes d'halogène, C_{1-4} halogénoalkyle ou C_{1-4} chloroalcoxy ;
R_2 est H, C_{1-8} alkyle saturé ou insaturé, C_{1-8} alkyle saturé ou insaturé substitué par halogéno, $-CH_2CH_2OCH_2CH_3$, $-CH_2CH_2OCH_3$, C_{1-4} alkylcarbonyle, C_{1-4} alkylsulfonyle, phényle, benzyle non substitué ou benzyle substitué par un ou plusieurs groupements choisis dans le groupe constitué par un atome d'halogène, C_{1-4} halogénoalkyle ou C_{1-4} chloroalcoxy ;
R_3 et R_4 sont choisis indépendamment parmi H, C_{1-6} alkyle, allyle, benzyle, C_{1-4} alcoxy-C_{1-4} alkyle, C_{1-4} alcoxycarbonyle, phénoxycarbonyle, C_{2-6} alcynyl-carbonyle, C_{2-3} alcénylcarbonyle, C_{3-6} cycloalkylcarbonyle, un groupement benzoyle non substitué ou un groupement benzoyle substitué par un ou plusieurs groupements choisis dans le groupe constitué par des atomes d'halogène, C_{1-4} alkyle, C_{1-4} halogénoalkyle, C_{1-4} alcoxy ou C_{1-4} alkylcarbonyle, furanecarbonyle ou N,N-diméthylaminocarbonyle ; ou R_3 et R_4 forment ensemble $-CH_2-CH_2-$, $-CH_2-CH_2-CH_2-$ ou $-CH_2-XR-CH_2-$, où X représente un hétéroatome ; R est un substituant sur X et est choisi parmi H, C_{1-6} alkyle, allyle, benzyle, phényle, C_{1-4} alcoxy-C_{1-4} alkyle, C_{1-4} alcoxycarbonyle, phénoxycarbonyle, C_{2-6} alcynylcarbonyle, C_{2-3} alcénylcarbonyle, C_{3-6} cycloalkylcarbonyle, un groupement benzoyle non substitué ou un groupement benzoyle substitué par un ou plusieurs groupements choisis dans le groupe constitué par des atomes d'halogène, C_{1-4} halogénoalkyle, C_{1-8} alkyle ou alcoxy saturé ou insaturé, ou C_{1-4} alkylcarbonyle, furanecarbonyle ou N,N-diméthylaminocarbonyle ;
R_5, R_6, R_7, R_8 et R_9 sont H, C_{1-4} alkyle saturé ou insaturé, halogène, C_{1-8} alcoxy saturé ou insaturé, C_{1-4} halogénoalcoxy saturé ou insaturé, C_{1-4} alkylcarbonyle, C_{1-4} alkylsulfonyle, phényle ou benzyle ;
Y est nitro, cyano, trifluorométhyle, trifluoroacétyle, ou trifluorométhylsulfonyle ; ou
le composé est le Composé n°71 ou le Composé n°73



Composé n°71



Composé n°73

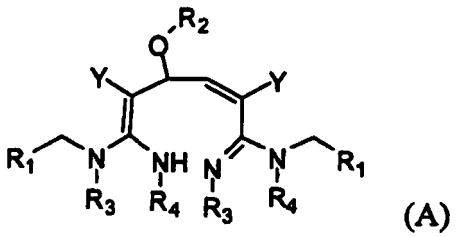
2. Composé, son isomère optique ou isomère cis,trans, ou ses sels acceptables sur le plan agrochimique selon la revendication 1, dans lequel R_1 est choisi parmi pyridyle, thiazolyle, pyrimidinyle, tétrahydrofuryle, oxazolyle, ou les groupements halogénés de ceux-ci.

3. Composé, son isomère optique ou isomère cis,trans, ou ses sels acceptables sur le plan agrochimique selon la revendication 1, dans lequel R_2 représente H, C_{1-4} alkyle saturé ou insaturé, C_{1-4} halogénoalkyle saturé ou insaturé, C_{1-4} alkylcarbonyle, benzyle non substitué ou benzyle substitué par un ou plusieurs groupements choisis dans le groupe constitué par un atome d'halogène, C_{1-4} halogénoalkyle ou C_{1-4} chloroalcoxy.

4. Composé, son isomère optique ou isomère cis,trans, ou ses sels acceptables sur le plan agrochimique selon la revendication 1, dans lequel R_3 et R_4 sont H, un groupement C_{1-6} alkyle, ou R_3 et R_4 forment ensemble - CH_2-CH_2- ou CH_2 - CH_2 - CH_2 - .

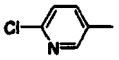
5. Composé, son isomère optique ou isomère cis,trans, ou ses sels acceptables sur le plan agrochimique selon la revendication 1, dans lequel R_5, R_6, R_7, R_8 et R_9 sont H, C_{1-2} alkyle saturé ou insaturé, halogène, C_{1-4} alcoxy saturé ou insaturé, C_{1-2} halogénoalcoxy saturé ou insaturé, ou C_{1-2} alkylsulfonyle.

6. Composé, son isomère optique ou isomère cis,trans, ou ses sels acceptables sur le plan agrochimique selon la revendication 1, **caractérisé en ce que** le composé est choisi dans le groupe constitué par les composés n°1-81 :

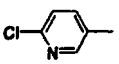


(A)

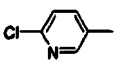
Composé n°1, où

R_1=  ;

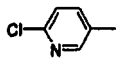
R_2= H ; R_3= C_2H_5 ; R_4= CH_3 ; et Y= NO_2 ;
Composé n°2, où

R_1=  ;

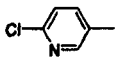
R_2= CH_3 ; R_3= C_2H_5 ; R_4= CH_3 ; et Y= NO_2 ;
Composé n°3, où

R_1=  ;

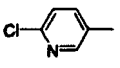
R_2= C_2H_5 ; R_3= C_2H_5; R_4= CH_3 ; et Y= NO_2 ;
Composé n°4, où

R_1=  ;

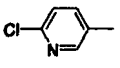
R_2= C_3H_7 ; R_3= C_2H_5 ; R_4= CH_3 ; et Y= NO_2 ;
Composé n°5, où

R_1=  ;

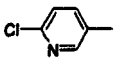
R_2= i-C_3H_7 ; R_3= C_2H_5 ; R_4= CH_3 ; et Y= NO_2 ;
Composé n°6, où

R_1=  ;

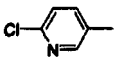
R_2= benzyle ; R_3= C_2H_5 ; R_4= CH_3 ; et Y= NO_2 ;
Composé n°7 , où

R_1=  ;

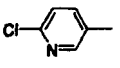
; R_2= H ; R_3= H ; R_4= CH_3 ; et Y= NO_2 ;
Composé n°8, où

R_1=  ;

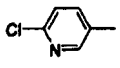
R_2 = CH_3 ; R_3= H ; R_4= CH_3 ; et Y= NO_2 ;
Composé n°9, où

R_1=  ;

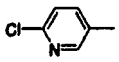
R_2= C_2H_5 ; R_3= H ; R_4= CH_3 ; et Y= NO_2 ;
Composé n°10, où

R_1=  ;

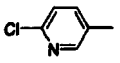
R2= C_3H_7 ; R_3= H ; R_4= CH_3 ; et Y= NO_2 ;
Composé n°11, où

R_1=  ;

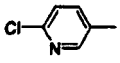
R_2= i-C_3H_7 ; R_3= H ; R_4= CH_3 ; et Y= NO_2 ;
Composé n°12, où

R_1=  ;

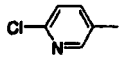
R_2= benzyle ; R_3= H ; R_4= CH_3 ; et Y= NO_2 ;
Composé n°13, où

R_1=  ;

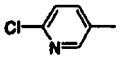
R_2= H ; R_3 et R_4 forment ensemble -CH_2-CH_2- ; et Y= NO_2 ;
Composé n°14, où

R_1=  ;

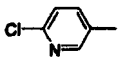
R_2= CH_3 ; R_3 et R_4 forment ensemble -CH_2-CH_2- ; et Y= NO_2 ;
Composé n°15, où

R_1=  ;

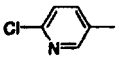
R_2= C_2H_5 ; R_3 et R_4 forment ensemble -CH_2-CH_2- ; et Y= NO_2 ;
Composé n°16, où

R_1=  ;

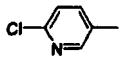
R_2= C_3H_7 ; R_3 et R_4 forment ensemble -CH_2-CH_2- ; et Y= NO_2 ;
Composé n°17, où

R_1=  ;

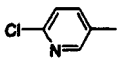
R_2= i-C_3H_7 ; R_3 et R_4 forment ensemble -CH_2-CH_2- ; et Y= NO_2 ;
Composé n°18, où

R_1=  ;

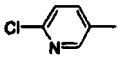
R_2= benzyle ; R_3 et R_4 forment ensemble -CH_2-CH_2- ; et Y= NO_2 ;
Composé n°19, où

R_1=  ;

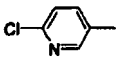
R_2= H ; R_3 et R_4 forment ensemble -CH_2-CH_2- ; et Y= CN ;
Composé n°20, où

R_1=  ;

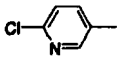
R_2= H ; R_3 et R_4 forment ensemble -CH_2-CH_2- ; et Y= CN ;
Composé n°21, où

R_1=  ;

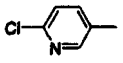
R_2= H ; R_3 et R_4 forment ensemble -CH_2-CH_2- ; et Y= CN ;
Composé n°22, où

R_1=  ;

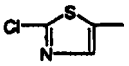
R_2= H ; R_3 et R_4 forment ensemble -CH_2-CH_2- ; et Y= CN ;
Composé n°23, où

R_1=  ;

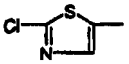
R_2= H ; R_3 et R_4 forment ensemble -CH_2-CH_2- ; et Y= CN ;
Composé n°24, où

R_1=  ;

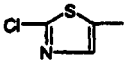
R_2= H ; R_3 et R_4 forment ensemble -CH_2-CH_2- ; et Y= CN ;
Composé n°25, où

R_1=  ;

R_2= H ; R_3 et R_4 forment ensemble -CH_2-CH_2- ; et Y= NO_2 ;
Composé n°26, où

R_1=  ;

R_2= H ; R_3 et R_4 forment ensemble -CH_2-CH_2- ; et Y= NO_2 ;
Composé n°27, où

R_1=  ;

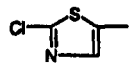
R_2= H ; R_3 et R_4 forment ensemble -CH_2-CH_2- ; et Y= NO_2 ;
Composé n°28, où

R_1=  ;

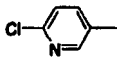
R_2= H ; R_3 et R_4 forment ensemble -CH_2-CH_2- ; et Y= NO_2 ;
Composé n°29, où

R_1=  ;

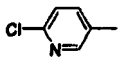
R_2= H ; R_3 et R_4 forment ensemble -CH_2-CH_2- ; et Y= NO_2 ;
Composé n°30, où

R_1=  ;

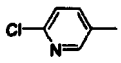
R_2= H ; R_3 et R_4 forment ensemble -CH_2-CH_2-CH_2- ; et Y= NO_2 ;
Composé n°31, où

R_1=  ;

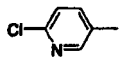
R_2= H ; R_3 et R_4 forment ensemble -CH_2-CH_2-CH_2- ; et Y= NO_2 ;
Composé n°32, où

R_1=  ;

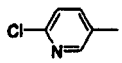
R_2= H; R_3 et R_4 forment ensemble -CH_2-CH_2-CH_2- ; et Y= NO_2 ;
Composé n°33, où

R_1=  ;

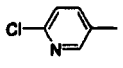
R_2= H ; R_3 et R_4 forment ensemble -CH_2-CH_2-CH_2- ; et Y= NO_2 ;
Composé n°34, où

R_1=  ;

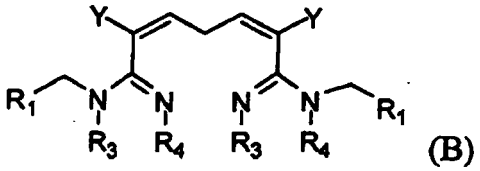
R_2= H ; R_3 et R_4 forment ensemble -CH_2-CH_2-CH_2- ; et Y= NO_2 ;
Composé n°35, où

R_1=  ;

R_2= H ; R_3 et R_4 forment ensemble -CH_2-CH_2-CH_2- ; et Y= NO_2 ;
Composé n°36, où

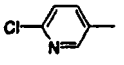
R_1=  ;

R_2= H ; R_3 et R_4 forment ensemble -CH_2-CH_2-CH_2- ; et Y= NO_2 ;

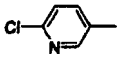


(B)

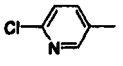
Composé n°37, où

R_1=  ;

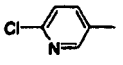
R_3= C_2H_5 ; R_4= CH_3 ; et Y= NO_2 ;
Composé n°38, où

R_1=  ;

R_3= H ; R_4= CH_3 ; et Y= NO_2 ;
Composé n°39, où

R_1=  ;

R_3 et R_4 forment ensemble -CH_2-CH_2- ; et Y= NO_2 ;
Composé n°40, où

R_1=  ;

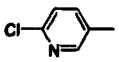
R_3 et R_4 forment ensemble -CH_2-CH_2- ; et Y= CN ;
Composé n°41, où

R_1=  ;

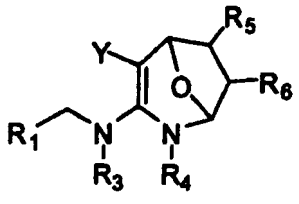
R_3 et R_4 forment ensemble -CH_2-CH_2- ; et Y= NO_2 ;
Composé n°42, où

R_1=  ;

R_3 et R_4 forment ensemble- CH_2-CH_2- ; et Y= NO_2 ;
Composé n°43, où

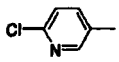
R_1=  ;

R_3 et R_4 forment ensemble -CH_2-CH_2-CH_2- ; et Y= NO_2 ;

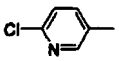


(C)

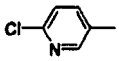
Composé n°44, où

R_1=  ;

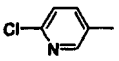
R_3= H ; R_4= CH_3 ; R_5= H ; R_6= H ; et Y= NO_2 ;
Composé n°45, où

R_1=  ;

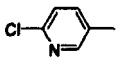
R_3= CH_3 ; i R_4= CH_3 ; i R_5= H ; R_6= H ; et Y= NO_2 ;
Composé n°46, où

R_1=  ;

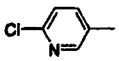
R_3= C_2H_5 ; R_4= CH_3 ; R_5= H ; R_6= H ; et Y= NO_2 ;
Composé n°47, où

R_1=  ;

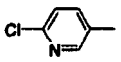
R_3= H ; R_4= H ; R_5= H ; R_6 = H ; et Y= NO_2 ;
Composé n°48, où

R_1=  ;

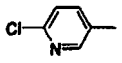
R_3= CH_3 ; R_4= H ; R_5= H ; R_6= H ; et Y= NO_2 ;
Composé n°49, où

R_1=  ;

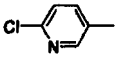
R_3= C_2H_5 ; R_4= H ; R_5= H ; R_6= H ; et Y= NO_2 ;
Composé n°50, où

R_1=  ;

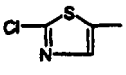
R_3= CH_3 ; R_4= C_2H_5 ; R_5= H ; R_6= H ; et Y= NO_2 ;
Composé n°51, où

R_1=  ;

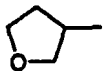
R_3= C_2H_5 ; R_4= C_2H_5 ; R_5= H ; R_6= H ; et Y= NO_2 ;
Composé n°52, où

R_1=  ;

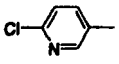
R_3 et R_4 forment ensemble -CH_2-CH_2- ; R_5= H ; R_6= H ; et Y= NO_2 ;
Composé n°53, où

R_1=  ;

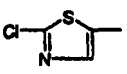
R_3 et R_4 forment ensemble -CH_2-CH_2- ; R_5= H ; R_6= H ; et Y= NO_2 ;
Composé n°54, où

R_1=  ;

R_3 et R_4 forment ensemble -CH_2-CH_2- ; R_5= H ; R_6= H ; et Y= NO_2 ;
Composé n°55, où

R_1=  ;

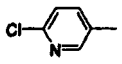
R_3 et R_4 forment ensemble- CH_2-CH_2- ; R_5= CH_3 ; R_6= CH_3 ; et Y= NO_2 ;
Composé n°56, où

R_1=  ;

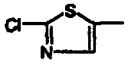
R_3 et R_4 forment ensemble -CH_2-CH_2- ; R_5= CH_3 ; R_6= CH_3 ; et Y= NO_2 ;
Composé n°57, où

R_1=  ;

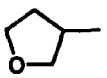
R_3 et R_4 forment ensemble -CH_2-CH_2- ; R_5= CH_3 ; R_6= CH_3 ; et Y= NO_2 ;
Composé n°58, où

R_1=  ;

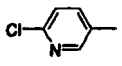
R_3 et R_4 forment ensemble -CH_2-CH_2- ; R_5= F ; R_6= F ; et Y= NO_2 ;
Composé n°59, où

R_1=  ;

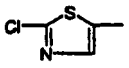
R_3 et R_4 forment ensemble -CH_2-CH_2- ; R_5= F ; R_6= F ; et Y= NO_2 ;
Composé n°60, où

R_1=  ;

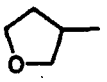
R_3 et R_4 forment ensemble -CH_2-CH_2- ; R_5= F ; R_6= F ; et Y= NO_2 ;
Composé n°61, où

R_1=  ;

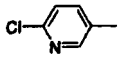
R_3 et R_4 forment ensemble -CH_2-CH_2-CH_2- ; R_5= H ; R_6= H ; et Y= NO_2 ;
Composé n°62, où

R_1=  ;

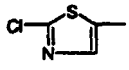
R_3 et R_4 forment ensemble -CH_2-CH_2-CH_2- ; R_5= H ; R_6= H ; et Y= NO_2 ;
Composé n°63, où

R_1=  ;

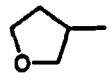
R_3 et R_4 forment ensemble -CH_2-CH_2-CH_2= ; R_5= H ; R_6= H ; et Y= NO_2 ;
Composé n°64, où

R_1=  ;

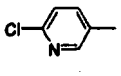
R_3 et R_4 forment ensemble -CH_2-CH_2- ; R_5= H ; R_6= H ; et Y= CN ;
Composé n°65, où

R_1=  ;

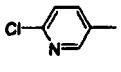
R_3 et R_4 forment ensemble -CH_2-CH_2- ; R_5= H ; R_6= H ; et Y= CN ;
Composé n°66, où

R_1=  ;

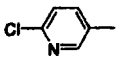
R_3 et R_4 forment ensemble -CH_2-CH_2- ; R_5= H ; R_6= H ; et Y= CN ;
Composé n°67, où

R_1=  ;

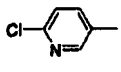
R_3 et R_4 forment ensemble -CH_2-CH_2- ; R_5= H ; R_6= CH_3O ; et Y= NO_2 ;
Composé n°68, où

R_1=  ;

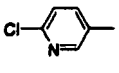
R_3 et R_4 forment ensemble -CH_2-CH_2- ; R_5= H ; R_6= C_2H_5O ; et Y= NO_2 ;
Composé n°69, où

R_1=  ;

R_3 et R_4 forment ensemble -CH_2-CH_2- ; R_5= CH_3O ; R_6= H ; et Y= NO_2 ;
Composé n°70, où

R_1=  ;

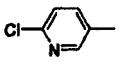
R_3 et R_4 forment ensemble- CH_2-CH_2- ; R_5= C_2H_5O ; R_6= H ; et Y= NO_2 ;
Composé n°71, où

R_1=  ;

R_3 et R_4 forment ensemble -CH_2-CH_2- ;

R_5=  ;

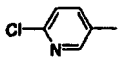
R_6= H ; et Y= NO_2 ;
Composé n°72, où

R_1=  ;

R_3 et R_4 forment ensemble -CH_2-CH_2- ;

R_5=  ;

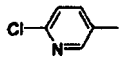
R_6= H ; et Y= NO_2 ;
Composé n°73, où

R_1=  ;

R_3 et R_4 forment ensemble -CH_2-CH_2- ; R_5= H ;

R_6=  ;

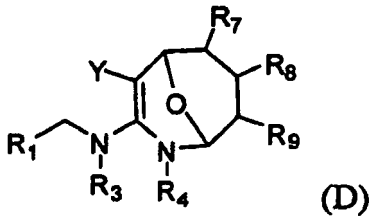
et Y= NO_2 ;
Composé n°74, où

R_1=  ;

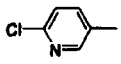
R_3 et R_4 forment ensemble -CH_2-CH_2- ; R_5= H ;

R_6=  ;

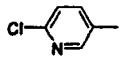
et Y= NO_2 ;


(D)

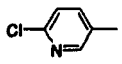
Composé n°75, où

R_1=  ;

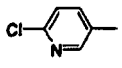
R_3= C_2H_5 ; R_4= CH_3 ; R_7=R_8=R_9= H ; et Y= NO_2 ;
Composé n°76, où

R_1=  ;

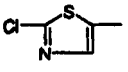
R_3= H ; R_4= CH_3 ; R_7=R_8=R_9= H ; et Y= NO_2 ;
Composé n°77, où

R_1=  ;

R_3 et R_4 forment ensemble -CH_2-CH_2- ; R_7=R_8=R_9= H ; et Y= NO_2 ;
Composé n°78, où

R_1=  ;

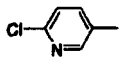
R_3 et R_4 forment ensemble -CH_2-CH_2- ; R_7=R_8=R_9= H ; et Y= CN ;
Composé n°79, où

R_1=  ;

R_3 et R_4 forment ensemble -CH_2-CH_2- ; R_7=R_8=R_9= H ; et Y= NO_2 ;
Composé n°80, où

R_1=  ;

R_3 et R_4 forment ensemble -CH_2-CH_2- ; R_7=R_8=R_9= H ; et Y= NO_2 ;
Composé n°81, où

R_1=  ;

R_3 et R_4 forment ensemble -CH_2-CH_2-CH_2- ; R_7=R_8=P_9= H ; et Y= NO_2.

7. Composé, son isomère optique ou isomère cis,trans, ou ses sels acceptables sur le plan agrochimique selon la revendication 1, dans lequel Y est un groupement nitro ou un groupement cyano.

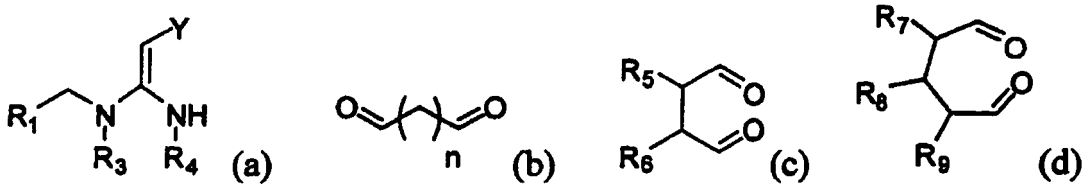
8. Composition agrochimique, comprenant:

(a) 0,001-99,99% en poids du composé, de son isomère optique, son isomère cis,trans, de ses sels acceptables sur le plan agrochimique selon l'une quelconque des revendications 1-7, ou une combinaison de ceux-ci ; et
(b) un véhicule ou excipient acceptable sur le plan agrochimique.

9. Utilisation de la composition agrochimique selon la revendication 8, pour tuer ou contrôler des nuisibles agricoles, des nuisibles présentant un risque pour la santé animale, et des nuisibles sanitaires ; ou l'utilisation de la composition agrochimique selon la revendication 8 comme composition insecticide pour tuer ou contrôler des nuisibles agricoles, des nuisibles sanitaires et des nuisibles présentant un risque pour la santé animale.

10. Méthode de préparation du composé, de son isomère optique ou isomère cis,trans, ou de ses sels acceptables sur le plan agrochimique selon l'une quelconque des revendications 1-7, **caractérisée en ce que** la méthode comprend les étapes suivantes :

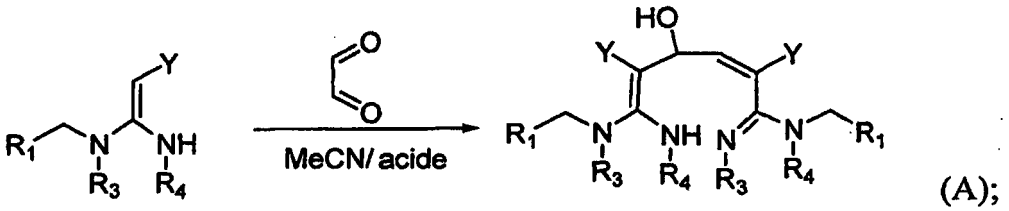
en présence d'un acide catalytique et à 0-60°C, la réaction d'un composé de formule (a) avec un composé (b), (c) ou (d), formant ainsi le composé (A), (B), (C) ou (D), où R_2 représente H



où R_1, R_3, R_4, R_5, R_6, R_7, R_8, R_9 et Y sont tels que définis selon la revendication 1, et n vaut 0 ou 1.

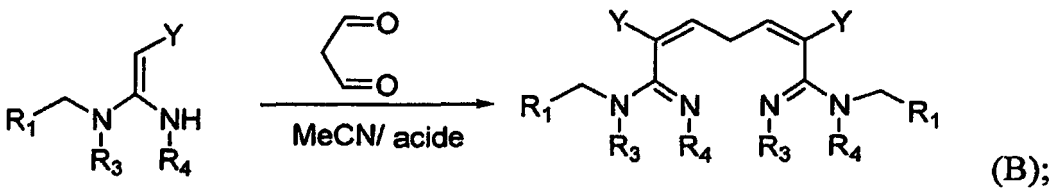
11. Méthode selon la revendication 10, **caractérisée en ce que** la méthode comprend:

en présence d'un acide catalytique, la réaction suivante est effectuée à 20-30°C dans de l'acétonitrile pendant 2-24 heures, formant ainsi le composé (A), où R_2 est H



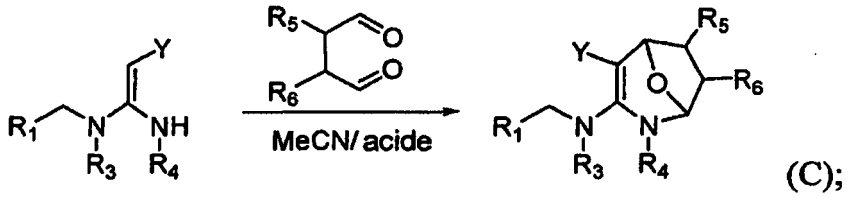
pp. 7 acid → acide

en présence d'un acide catalytique, la réaction suivante est effectuée à 20-30°C dans de l'acétonitrile pendant 2-24 heures, formant ainsi le composé (B)



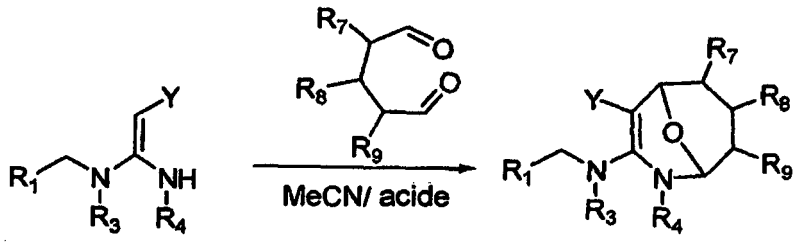
pp. 8 acid → acide

en présence d'un acide catalytique, la réaction suivante est effectuée à 10-50°C dans de l'acétonitrile pendant 2-24 heures, formant ainsi le composé (C)



pp. 8 acid → acide

en présence d'un acide catalytique, la réaction suivante est effectuée à 10-50°C dans de l'acétonitrile pendant 2-24 heures, formant ainsi le composé (D)



(D).

pp. 8 acid → acide

REFERENCES CITED IN THE DESCRIPTION

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